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INTRODUCTION TO
THEORETICAL ORGANIC CHEMISTRY
by
P. H. HERMANS, PH. D.
(Utrecht, The Netherlands)

Edited and revised by R. E. REEVES, PH. D.
(New Orleans, La., U.S.A.)

This is a systematic treatise in theoretical chemistry with the emphasis on organic chemistry and organic reactions. In this respect it differs (with a minimum of mathematical formulae) from all other books on theoretical chemistry, for in the past the broad scope of theoretical chemistry has always been approached from the point of view of general chemistry or physical chemistry. It compares with the several excellent theoretical, physical chemistry books, but the emphasis here is upon organic chemistry. It is stimulating and informative, and will provide the organic chemist with the theoretical knowledge which he so greatly needs, but which in the past has never been assembled in a comprehensive volume such as this.

6 × 9 xii and 507 pages 79 illus. 50 tables 1954

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Col. = Colorimetric, heterometric, photometric and spectrophotometric analysis — colorimétrie, hétérométrie, photométrie et spectrophotométrie — heterometrische, kolorimetrische, photometrische und spektrophotometrische Analyse
El. = Electrical methods (except polarography) — Méthodes électriques (excepté polarographie) — Elektrische Methoden (mit Ausnahme Polarographie)
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ERRATA

Anal. Chim. Acta, Vol. 11 (1954).
p. 396, line 3 from bottom, last word "vor" should read "nach".
p. 397, in Table I, line 2, for 100 ml read 20 ml.
in Table I, line 3, for 20 c_0 read 100 c_0.
p. 520, in Table VII, third column, lines 4, 5 and 6 should read 0.01N, 0.01N and 0.001N respectively.
p. 520, line 6 above formula, for page 572 read page 512.

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A RAPID IODOMETRIC METHOD FOR THE DETERMINATION OF COPPER AND ZINC

by

S. Z. HAIDER AND M. H. KHUNDKAR

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Chemical methods available for the determination of zinc in the presence of copper, require that the latter be separated first or rendered ineffective through complex formation. The usual method is to separate copper as cuprous sulphocyanide. DUCRET[1] recommended separation of copper with salicylaldoxime. EVANS[2], on the other hand, formed a soluble complex of copper with KCN that did not interfere with the latter precipitation of ZnS. RAY[3] observed that if copper is converted into the thiourea complex, zinc can be separated as its quinaldinate, which is determined gravimetrically.

In none of the above processes, can copper and zinc be determined in the same solution. The present work reports the determination of both copper and zinc iodometrically in such a case, the principle of the method being based on earlier investigations[4] for the iodometric determination of ferricyanide in presence of zinc, utilizing the reaction:

$$2\ K_3[Fe(CN)_6] + 2\ KI \rightarrow 2\ K_4[Fe(CN)_6] + I_2$$

Zinc captures the ferrocyanide by complex formation as it is formed, thus helping a quantitative progress of the reaction towards the right.

In determining zinc in admixture with copper by the proposed method, the conventional iodometric determination of copper is unsatisfactory, because the cuprous iodide (or the iodide complex) tends to react with potassium ferricyanide to liberate some iodine, and brown copper ferrocyanide is also formed. The determination of zinc is not possible under such conditions. This difficulty has also been evaded in the present investigation by adopting BRUHNS[5] 's modification, which uses sufficient KCNS and a small amount of KI for iodometric determination of copper.

$$2\ Cu^{+2} + 4\ I^- \rightarrow Cu_2I_2 + I_2$$
$$Cu_2I_2 + 2\ (CNS)^- \rightarrow Cu_2(CNS)_2 + 2\ I^-$$
$$2\ Cu^{+2} + 4\ (CNS)^- \rightarrow 2\ Cu(CNS)_2$$
$$2\ Cu(CNS)_2 + 2\ S_2O_3^{-2} \rightarrow Cu_2(CNS)_2 + 2\ (CNS)^- + S_4O_6^{-2}$$

The basis of MOHR's method[4] is to have iodine liberated in fairly acid solution (in the presence of excess of zinc) in quantitative equivalence of the ferricyanide present. If it is desired to effect the liberation of iodine according to the equation

$$2\ K_3[Fe(CN)_6] + 2\ KI + 3\ ZnSO_4 \rightarrow K_2Zn_3[Fe(CN)_6]_2 + K_2SO_4 + I_2$$

i.e. in quantitative equivalence of zinc, a condition has to be maintained so that the ferricyanide itself may not liberate iodine from KI. It has been observed that this is possible by proper choice of acid. The probable influence of $Cu_2(CNS)_2$ (which would be present during titration of zinc according to the proposed method) was also taken into consideration.

5 g of $CuSO_4.5H_2O$ were dissolved in 150 ml of water and a solution containing 10 g of KCNS in presence of sufficient excess of sulphurous acid was added. The $Cu_2(CNS)_2$ precipitate was washed free from sulphurous acid and the precipitate was transferred to a 250 ml measuring flask. 10 ml portions of the suspension were withdrawn (after thorough shaking) each time, and transferred to a 250 ml conical flask containing about 70 ml water. 1 ml of 0.2*M* potassium ferricyanide solution was added to it from a burette, followed by 5 ml of 10% KI solution. The solution was allowed to stand for exactly 20 min after which the liberated iodine was titrated with *N*/50 thiosulphate solution. Results are given in Table I.

TABLE I

INFLUENCE OF DIFFERENT ACIDS ON THE LIBERATION OF IODINE FROM KI BY POTASSIUM FERRICYANIDE IN PRESENCE OF CUPROUS SULPHOCYANIDE PPT

Acid	Concn.	Vol. of acid added ml	0.02*N* $Na_2S_2O_3$ reqd. ml
HCl	2*M*	5.0	3.60
		10.0	4.85
H_2SO_4	*M*	5.0	3.25
		10.0	4.10
H_3PO_4	2*M*	10.0	0.40
		20.0	0.80
CH_3COOH	2*M*	10.0	0.35
		20.0	0.60
$H_2C_2O_4$	*M*	10.0	0.25
		20.0	0.55
No acid added	—	—	nil
	—	—	0.10
	—	—	nil

It is thus quite clear that potassium ferricyanide is ineffective towards KI (and thus would be suitable for the iodometric determination of zinc) in neutral solution even if the precipitate of $Cu_2(CNS)_2$ is present. Oxalic, acetic or phosphoric acid present in small quantities would not create much difficulty, but hydrochloric or sulphuric acid must be avoided. Obviously nitric acid must be avoided.

In order to confirm how these acids would actually behave in presence of both copper and zinc, the second set of experiments was carried out as follows.

To the mixture containing copper and zinc, KI was added (1 g/g of Cu), thoroughly shaken and then KCNS (8 g/g of Cu). After diluting to a total volume of 100 ml, the liberated iodine was titrated with standard thiosulphate solution. A known volume of the desired acid is then added followed by potassium ferricyanide solution in 1 ml portions. To facilitate the reaction, the liberated iodine is titrated as it is formed. For the sake of comparison, blank experiments were carried out taking the same proportions of zinc without any foreign precipitate or acid. Results are incorporated in Table II.

TABLE II

INFLUENCE OF DIFFERENT ACIDS ON THE IODOMETRIC DETERMINATION OF ZINC IN PRESENCE OF COPPER

Acid added	Concn. of acid	Vol. of acid added ml	$0.1N$ $Na_2S_2O_3$ ml	$0.1N$ reqd. $Na_2S_2O_3$ for blank (*i.e.* Zn without acid or Cu) ml
HCl	$2M$	5.0	14.10	13.20
		10.0	14.50	
H_2SO_4	M	5.0	13.60	13.15
		10.0	13.90	
H_3PO_4	M	10.0	13.10	13.20
		20.0	13.25	
CH_3COOH	$2M$	10.0	11.55	13.20
		20.0	11.90	
$H_2C_2O_4$	M	10.0	11.95	13.25
		20.0	12.30	

From the above observations it may be inferred that the addition of mineral acids leads to higher results. This is because the reaction between ferricyanide and potassium iodide in the presence of mineral acids gives an indistinct end-point. Low results in the presence of organic acids, such as acetic or oxalic acids, are possibly due to suppression of the main reaction towards the end of the titration. This has been confirmed by using citric and tartaric acids, in which cases the liberation of iodine was very slow. Phosphoric acid gives the best results and hence in the method finally adopted this has been used to effect neutralization of the mixed solution of copper and zinc if required.

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Final procedure for the determination of Cu and Zn from a solution containing their mixture

A mixture containing the desired proportions of Cu and Zn was taken. The free acid (if any) was neutralized by adding dilute NaOH solution till a permanent precipitate or turbidity remained. A drop or two of dilute phosphoric acid was added to dissolve the precipitate completely. Potassium iodide was added (1g/g Cu) and thoroughly shaken to precipitate Cu_2I_2. This was followed by addition of potassium sulphocyanide (8 g/g Cu) and titration of the liberated iodine with a standard 0.1N thiosulphate solution, until most of the iodine reacted. It was diluted with 50-60 ml water, 2 ml of starch solution were added and the titration for Cu was completed. 4 g K_2SO_4 and 3-4 g KI were added, and then 0.2M potassium ferricyanide solution, in 1 ml portions, was added gradually from a burette placed alongside the thiosulphate burette. Each time the liberated iodine was titrated to decolourization. Towards the end the addition of ferricyanide solution was controlled and regulated by stepping down to 0.5 ml portions, till the blue colour was no longer produced. A large excess of the ferricyanide was avoided and the addition was stopped when the solution turned yellow. Titration was judged to be complete when the blue colour did not reappear after waiting for about 30 seconds.

The results are calculated on the basis of 1 ml N $Na_2S_2O_3$ equivalent to 0.0990 g Zn, a factor about 1% higher than the theoretical one. The results are shown in Table III.

TABLE III

IODOMETRIC SIMULTANEOUS DETERMINATION OF Cu AND Zn

Copper taken g	Copper found g	Zinc taken g	0.1N $Na_2S_2O_3$ for Zn ml	Zinc found g	Error for Zn %
0.0193	0.0191	0.0654	6.60	0.0654	nil
		0.1308	13.20	0.1307	—0.1
		0.1635	16.45	0.1629	—0.5
0.0395	0.0397	0.0654	6.65	0.0659	+0.7
		0.1308	13.25	0.1312	+0.3
		0.1635	16.45	0.1629	—0.5
0.0983	0.0986	0.0654	6.55	0.0649	—0.7
		0.1308	13.20	0.1307	—0.1
		0.1635	16.55	0.1638	+0.2

The use of both KCNS and KI for the precipitation of copper was found most suitable, as in the presence of KI (excess) the precipitate of cuprous iodide has

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a tendency to dissolve and form a complex. When the titration of zinc is carried out under these conditions a brown precipitate is obtained on the addition of ferricyanide solution, and titration is not possible. Again if only KCNS is used to precipitate copper as $Cu_2(CNS)_2$ in the presence of sufficient H_2SO_3 or $NaHSO_3$, it will naturally entail disadvantages such as prolonged boiling (with acid if necessary) to remove excess of SO_2, which does not permit simultaneous determination of both Cu and Zn in the same solution. The present modification makes it possible to finish the determination of both Cu and Zn in a sample solution in 15 min.

SUMMARY

A method has been described for the iodometric simultaneous determination of zinc and copper. Copper is determined in the presence of sufficient KCNS and a small amount of KI. This is followed by the titration of the iodine equivalent to the zinc, which is liberated by the addition of potassium ferricyanide solution.

Interference is eliminated completely by keeping the solution neutral or just acid with phosphoric acid.

Within the range under investigation, results are obtained which are accurate to ± 0.7 %.

RÉSUMÉ

Une méthode est décrite pour doser simultanément le zinc et le cuivre par iodométrie. Le cuivre est déterminé en présence de KCNS et d'une petite quantité de KI. On titre ensuite l'iode équivalent au zinc, libéré par addition d'une solution de ferricyanure de potassium. Les interférences sont éliminées si l'on travaille en solution neutre ou légèrement acidifiée par l'acide phosphorique. Les auteurs sont arrivés à une précision de 0.7 %.

ZUSAMMENFASSUNG

Es wird eine iodometrische Methode beschrieben für die gleichzeitige Bestimmung von Zink und Kupfer. Das Kupfer wird bestimmt in Gegenwart vor KCNS und von einer geringen Quantität von KJ. Man titriert dann das Iode, welches dem Zink äquivalent ist und durch Zusatz von einer Lösung von Kaliumferricyanid gebildet wurde. Die gegenseitigen Beeinflussungen werden ausgeschaltet, wenn man in neutraler oder mit Phosphorsäure leicht angesäuerter Lösung arbeitet. Die Autoren erhalten eine Präzision von 0.7 %.

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A RAPID VOLUMETRIC METHOD FOR THE DETERMINATION OF BERYLLIUM IN BERYLS AND ASSOCIATED MINERALS

by

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The purpose of the present investigation was to develop a quick and simple method for the determination of beryllium in beryl, generally associated with the minerals of pegmatite origin.

Beryllium is usually determined either by gravimetric or photometric methods. In the gravimetric methods it is estimated either as oxide[1,2,3,4,5] or as phosphate[6]. Particular mention may be made of the phosphate method, wherein beryllium is precipitated as beryllium ammonium phosphate and ignited and weighed as $Be_2P_2O_7$, interfering elements being kept in solution with complexone II. The photometric methods make use of either the colour reactions or fluorescence of Be^{+2} with organic reagents[7,8,9,10,11,12,13,14,15,16].

While there has been considerable development, particularly in the latter field, the analytical chemistry of beryllium is conspicuous by the absence of a good volumetric procedure. The only one reported so far is based on the following reactions[17]. Beryllium, precipitated quantitatively as $Be(OH)_2$ at pH 8.5, when treated with an alkali fluoride, liberates two equivalents of alkali which may be titrated acidimetrically. Evidently, a host of other elements react similarly, so that all of them must either be absent, or their concentrations accurately known in order that suitable corrections may be applied. Even when such corrections are possible, the method is essentially empirical, the reaction between $Be(OH)_2$ and fluoride not being stoichiometric[16].

The present paper describes a volumetric method in which beryllium is precipitated under suitable conditions as beryllium ammonium phosphate, and determined indirectly by titrating its equivalent phosphate against standard bismuthyl perchlorate.

METHOD

The method consists essentially of two steps:

1. Precipitation of beryllium as beryllium ammonium phosphate. The method

of HURÉ and co-workers (*loc. cit*) has been followed with certain minor modifications as described below.

2. Titration of the equivalent phosphate. Here, advantage is taken of the fact that bismuthyl perchlorate reacts in acidic solutions with orthophosphate to give a precipitate of $BiPO_4$, and that excess bismuth, over the stoichiometric ratio can be detected by the orange yellow color produced with a chloroform solution of diallyldithiocarbamidohydrazine. SUBBARAMAN has employed this reaction for the determination of phosphate in certain fertilizers[18].

Reagents

1. Complexone II. A 10% aqueous solution was prepared from the disodium salt (B.D.H.LR).

2. 20% aqueous solution of diammonium hydrogen phosphate (B.D.H. AnalaR).

3. Diallyldithiocarbamidohydrazine. The reagent was prepared according to the method of FREUND AND WISCHIWIANSKY[19]. 21 g of hydrazine hydrochloride were mixed with 21 g of Na_2CO_3 and as much water added as was necessary to dissolve the alkali. The solution was mixed with 40 g of allyl mustard oil dissolved in 160 g of alcohol and the mixture refluxed over a water bath for 1½ hours. On cooling, the carbamidohydrazine separated out in glistening flakes which were collected and recrystallized from hot alcohol.

A saturated solution of the substance in chloroform — henceforth designated as 'reagent' — was used as indicator in the titration.

4. Standard bismuthyl perchlorate. An approximately $M/20$ solution was prepared by evaporating to fumes 24 g of bismuth nitrate with 6 ml of 60% perchloric acid. The residue was dissolved in distilled water and made up to 1 litre.

5. 6% dilute perchloric acid — 100 ml of 60% acid diluted to 1 litre.

6. Wash liquid for beryllium ammonium phosphate. 2% ammonium nitrate solution adjusted to pH $\simeq$ 5 with ammonium acetate in presence of bromocresol green.

7. Indicator solution. 0.05% solution of bromocresol green (pH 3.8-5.4) in 50% alcohol.

8. $2N$ ammonium acetate.

Standardization of bismuth solution

The bismuth content of the perchlorate solution was determined by precipitating from an aliquot as phosphate, igniting and weighing as $BiPO_4$ according to the standard procedure[3]. The results were checked independently by titration against standard $M/20$ potassium dihydrogen phosphate as described below and found to be in good agreement.

Effect of acidity and the presence of beryllium on the titration

The acidity of the phosphate solution has an important bearing on the titration of phosphate with standard bismuth. While bismuth phosphate is quantitatively precipitated from 1-2% nitric acid, the extraction of bismuth by the reagent into the chloroform phase is sensitive to the acidity of the aqueous phase. SHARMA AND GUPTA[20] mentioned that the optimum pH for the extraction is 2·4—2·7 and that it is independent of the excess of the reagent. Hence this pH range will be ideal so far as the end-point is concerned; but it is not suitable for the determination of phosphate derived from beryllium ammonium phosphate, since at pH $>$ 2 beryllium starts precipitating as phosphate. The following experiments were carried out to determine the optimum acidity for the titration.

Aliquots of beryllium perchlorate solution in dilute perchloric acid, corresponding to 22 mg of beryllium oxide were added to 20 ml aliquots of standard $M/20$ potassium hydrogen phosphate. The solutions were neutralized with dilute ammonia (1 : 1) to a faint cloudiness, which was removed by adding the minimum amount of dilute perchloric acid. Varying amounts of dilute perchloric acid were then added in excess, the solutions diluted to 100 ml and the phosphate titrated against standard bismuth in the presence of 10 ml of the reagent solution.

At a low acidity, the reaction was slow; increase of acid above 5 ml of dilute perchloric acid gave higher titres, and the end-point was found to be variable. As a result of a number of determinations 3-4 ml of dilute perchloric acid, added after the initial adjustment, was found to give very good results. The pH of such a solution was found to be $\simeq$ 1.8. Occasionally during the titration, a yellow color developed in the chloroform layer which disappeared after shaking vigorously or warming slightly. Titration of the warm phosphate solution (40-50°C) improved the speed of the reaction. Towards the end-point, the chloroform solution developed a persistant, uniform orange yellow tint as distinct from the oily yellow color which occasionally developed in the early stages. Furthermore, when hot solutions were titrated, the white $BiPO_4$ coagulated and settled very rapidly, particularly at the end-point.

The results of these experiments are given in Table I.

TABLE I

EFFECT OF ACIDITY ON THE TITRATION

Strength of bismuth solution: 0.0506M

Vol. of $M/20$ phosphate ml	Vol. of beryllium perchlorate ml	Vol. of dilute perchloric acid — ml	Titre value ml	Remarks
20	5	1	19.2	Reaction very slow
20	5	2	19.35	,,
20	5	4	19.50	End-point sharp and reaction was rapid
20	10	4	19.45	,,
20	10	3	19.50	,,
20	5	6	20.25	End-point variable; reaction very rapid

Determination of beryllium

When precipitated under proper conditions, beryllium phosphate conforms strictly to the formula $BeNH_4PO_4.6H_2O$[21]. HURÉ and others have also stressed the importance of obtaining the precipitate in a granular form. This was achieved by keeping a concentration of 1% phosphate in the supernatant liquor by adding 10 ml of 20% diammonium hydrogen phosphate to a solution of beryllium adjusted to a pH of 5 to 5.5 in a final volume of about 200 ml. The pH was adjusted using bromocresol green as indicator.

Acid solutions of beryllium were first neutralized in the presence of the required amount of phosphate, with dilute ammonia to a cloudiness which was removed by adding a few drops of dilute hydrochloric acid. Finally, 2*N* ammonium acetate was added till the indicator changed to a distinct blue color. For a final volume of about 200 ml approximately 25 ml of ammonium acetate were required, slight changes in the amount of ammonium acetate having little effect on the pH. The solution was then heated to boiling and left to granulate on a waterbath for ½ hour. The fine, granular precipitate was filtered through a close texture filter paper, and the beaker and filter paper were washed thoroughly with the wash solution to remove excess phosphate. The precipitate was washed down into the beaker with a jet of water and the filter paper rinsed thoroughly with 15 ml dilute perchloric acid and made up to a definite volume, and suitable aliquots were titrated against standard bismuth solution as described above. The accuracy of the procedure is evident from the values given in Table II.

TABLE II

DETERMINATION OF BERYLLIUM

Strength of bismuth solution: 0.0506*M*

Amount of beryllium oxide taken mg	Titre value	Beryllium oxide obtained mg	Error mg
25	19.5	24.7	— 0.3
30	23.75	30.10	+ 0.10
	23.80	29.95	— 0.05

Analysis of beryls

0.5 g of the ore was fused with Na_2CO_3 and the mineral brought completely into solution after removal of SiO_2 by the usual methods of silicate analysis. The beryllium was directly precipitated from the solution in the same way as described in the determination of beryllium with the only difference that 10 ml of the complexone solution were added to mask all the interfering elements. The

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precipitate of beryllium ammonium phosphate was filtered by decantation, dissolved in a small volume of hot dilute hydrochloric acid and reprecipitated, this time adding only 5 ml of complexone and 5 ml of phosphate solution for a final volume of about 100 ml. After granulation, the precipitate was filtered, washed thoroughly, dissolved in 15 ml of dilute perchloric acid and the solution made up to 250 ml. 100 ml aliquots were taken from the solution and titrated against standard bismuth solution. From the titre values the beryllium oxide content was calculated from the relation

1 ml M bismuth ≡ 25.02 mg beryllium oxide.

The results obtained for a number of standard beryl samples are given in Table III.

TABLE III

DETERMINATION OF BERYLLIUM OXIDE IN BERYLS

Sample No	% beryllium oxide obtained by standard procedures	% beryllium oxide obtained by present method	Difference
1	(12.05 (12.06*	12.23) 12.10)	+ 0.1
2	(12.20 (12.12*	12.34	+ 0.17
3	(12.85 (12.88*	12.72	— 0.04
4	6.54	6.77	+ 0.23
5	6.40	6.58	+ 0.18
6	(13.30 (13.28	13.35	+ 0.05
7	10.2	10.13	— 0.07
8	12.45	12.53	+ 0.08

* Results obtained from an outside laboratory.

CONCLUSION

The proposed method has the following advantages:

1. As it is a volumetric method, the difficult operation of igniting $BeNH_4PO_4.6H_2O$ to $Be_2P_2O_7$ (which needs meticulous attention to detail to obtain the white pyrophosphate of the correct composition) is avoided. Also, small amounts of residual silica, carried over in the separation, do not interfere in the titration.
2. Owing to its wide occurrence, small amounts of TiO_2 may be present in the

samples, which normally would be precipitated as phosphate, since titanium does not form a strong complex with complexone. We have been able to eliminate its interference by adding hydrogen peroxide before the precipitation of phosphate.

3. Its advantage over the classical procedures is the ease of operation, since no prior separations of the common interfering elements are required and so a considerable saving of time is achieved.

SUMMARY

A new volumetric method has been proposed for the determination of beryllium in beryls and associated minerals. The method involves the direct precipitation of beryllium as $BeNH_4PO_4.6H_2O$ in presence of complexone II, dissolving the precipitate in dilute perchloric acid and titrating the liberated phosphate with standard bismuthyl perchlorate. Results for samples agree within ± 0.2% of the standard values.

RÉSUMÉ

Une nouvelle méthode volumétrique est proposée pour le dosage du béryllium dans des béryls et autres minerais. Ce procédé consiste à précipiter directement le béryllium comme $BeNH_4PO_4.6H_2O$, en présence de complexon II, puis à dissoudre le précipité formé dans l'acide perchlorique et à titrer le phosphate libéré par une solution étalon de perchlorate de bismuthyle. Les résultats obtenus varient de ± 0.2 %.

ZUSAMMENFASSUNG

Es wird eine neue Methode beschrieben für die Bestimmung von Beryllium in Beryl und andern Mineralien. Bei diesem Verfahren wird das Beryllium direkt ausgefällt als $BeNH_4PO_4.6H_2O$ in Gegenwart von Komplexon II. Der so gebildete Niederschlag wird in Perchlorsäure aufgelöst und das freigelegte Phosphat wird mit einer bekannten Lösung von Bismutylperchlorat titriert. Die auf diese Weise erhaltenen Resultate weichen höchstens ± 0.2 % ab.

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THE MICRO-VOLUMETRIC DETERMINATION OF LEAD WITH THIONALIDE AND ITS APPLICATION TO THE ANALYSIS OF TIN-BASE AND LEAD-BASE ALLOYS

by

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INTRODUCTION

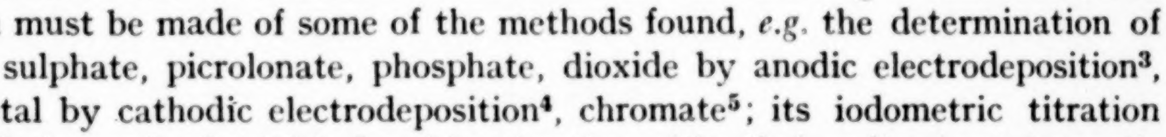
In the course of our systematic search for suitable micro-determinations of the constituents of tin-base and lead-base alloys[1,2], the existing micro-methods for the determination of lead were reviewed. Without enumerating all the references, mention must be made of some of the methods found, *e.g.* the determination of lead as sulphate, picrolonate, phosphate, dioxide by anodic electrodeposition[3], lead metal by cathodic electrodeposition[4], chromate[5]; its iodometric titration after isolation as lead sulphite[6] and its titration with ethylenediamine tetraacetic acid[7,8].

Few of these methods, however, had been applied to alloy analysis; *e.g.* GAPCHENKO applied his iodometric method[6] to alloys containing tin, antimony, lead and copper[9], and MILLER AND CURRIE determined lead as chromate in white metals, fusible alloys, tin-free copper-base alloys and bronzes[10].

After completion of the above-mentioned review, it was still deemed desirable to evolve an exact micro-volumetric method for the determination of lead with thionalide (thioglycollic acid, β-aminonaphthalide), based on BERG's[11] macro-method, with the intention of applying it later to the analysis of alloys.

Principle of method:

Lead cation is precipitated in a sodium carbonate solution, containing potassium cyanide and sodium tartrate, with an acetone solution of thionalide:

I. 2 

$$2\ C_{10}H_7\text{—}\underset{H}{N}\text{—}\underset{O}{\overset{}{C}}\text{—}CH_2SH + Pb^{+2} \longrightarrow (C_{10}H_7NHCOCH_2S)_2Pb + 2H^+$$

The washed precipitate is dissolved in a mixture of acetic acid and sulphuric acid. The liberated thionalide is oxidized with standard iodine solution to dithionalide:

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2. $2C_{10}H_7NHCOCH_2SH + I_2 \longrightarrow C_{10}H_7NHCOCH_2\text{–}S\text{–}S\text{–}CH_2CONHC_{10}H_7 + 2HI$

Lead is calculated from the volume of iodine solution participating in reaction 2.

With a view to acquiring familiarity both with this organic reagent and this method, determination of lead with thionalide was at first attempted on the macro-scale, following BERG's[11] directions.

Considerable difficulties presented themselves, such as the very tedious filtration of the lead thionalide precipitate, the more tedious washing of the precipitate, the difficulty of removing the washed precipitate quantitatively from the filter paper, the large volume of acid necessary to effect complete solution of the precipitate and the unsatisfactory end point. The results obtained by the above method were erratic and far from accurate.

It was, therefore, considered imperative to conduct a systematic study of all the factors affecting this determination, in order to remove the difficulties encountered and to obtain accurate results. It was felt that some of the difficulties would be eliminated by working on a micro-scale and employing a micro-technique; the experiments on the macro-scale were, therefore, abandoned and the elaboration of a micro-method was attempted forthwith.

The experiments leading towards this goal are given in the following text.

EXPERIMENTAL

Reagents and standard solutions employed were:

1. Lead nitrate solution (prepared by dissolving 1 g of pure lead metal in conc. nitric acid, evaporating excess acid and making up to 1 litre with bi-distilled water. The solution therefore contained 1 mg lead per ml).
2. 1% Phenolphthalein (alcoholic solution).
3. Sodium carbonate solution 2*N*.
4. Ammonium hydroxide, conc.
5. Potassium cyanide.
6. Sodium potassium tartrate.
7. Thionalide.
8. Acetone.
9. Acetone-water (mixture 1:1).
10. Glacial acetic acid-sulphuric acid 2*N* (mixture 3:1).
11. Carbon dioxide gas from a Kipp Apparatus, purified by bubbling it through a saturated solution of sodium bicarbonate.
12. Potassium iodide.
13. Standard 0.01*N* potassium iodate-iodide solution (prepared by dissolving 0.3567 g KIO_3 in 200 ml H_2O containing 1 g NaOH and 2-3 g KI, and making up to 1 litre).

14. Standard 0.02N potassium iodate-iodide solution (prepared by dissolving 0.7134 g KIO_3 in 200 ml H_2O containing 1 g NaOH and 2-3 g KI, and making up to 1 litre).
15. 1% starch solution.
16. Standard 0.01N sodium thiosulphate solution (prepared by diluting 0.1N solution and checked against Reagent No. 13).
17. Ammonium acetate solution, 40%.
18. Sodium acetate solution, 40%.
19. Alcohol-water (mixture 1:1).
20. Sulphuric acid, 10%.
21. Bi-distilled water was used throughout.

Tentative procedure

For a first tentative approach, BERG's[11] procedure, with slight modifications, was scaled down to 5 mg of lead, using a micro-technique. The procedure used was as follows: to the slightly acid solution of lead nitrate (5 mg lead in 5 ml), contained in a 30 ml Pyrex glass beaker, about 100 mg sodium potassium tartrate, 1 drop phenolphthalein solution and a sufficient quantity of sodium carbonate solution to neutralize the acid were added. About 200 mg of potassium cyanide were introduced next. The volume of the solution was now doubled by the addition of 2N sodium carbonate solution. 40-50 mg of thionalide, freshly dissolved in 1-2 ml of acetone, were now added dropwise with continuous stirring, the mixture heated to boiling with stirring, and allowed to cool. Boiling clarifies the milky solution. The yellow precipitate was then filtered through a filterstick of Pyrex glass (fine porosity)*, and beaker, stick and precipitate washed with water to remove all cyanide, and then with acetone- water (mixture 1:1) to remove excess of thionalide. The absence of cyanide was tested for with silver nitrate or with picric acid, while the iodine test was applied to ascertain the absence of thionalide.** The washed precipitate was then dissolved in about 20 ml of an acetic acid-sulphuric acid mixture (Reagent No. 10). This was at first effected by mechanical removal of the precipitate from the filterstick and by sucking the dissolving mixture back and forth through the filterplate to clean it. The solution, containing the dissolved thionalide and the suspended lead sulphate, was transferred to a 100 ml Erlenmeyer flask, some potassium iodide was added, and the thionalide titrated with standard 0.01N potassium iodate-iodide solution, until excess iodine was apparent from the yellow colour of the solution. The mixture was next diluted with water and back-titrated with a standard 0.01N sodium thiosulphate solution, using starch as indicator.

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* The dimensions of the filterstick used were: overall diameter: 10 mm; outside stem diameter: 4 mm; overall height: 110 mm. All filtersticks used were U.S.A. produce, made by Corning Glass Works.

** A sample of the wash liquid is diluted two times with water, acidified with sulphuric acid and an iodine solution added. If thionalide is present, a white precipitate of dithionalide is formed.[12]

DISCUSSION I

The procedure outlined above had a number of obvious faults which led to erratic results of the order of 10%, with the majority of results on the minus side. The faults, and the means adopted for their removal, in the order of their appearance in the procedure, were as follows:

1. Addition of the sodium carbonate to the lead solution in order to neutralize it, sometimes causes the appearance of a white precipitate, ranging from a faint turbidity to a precipitate of considerable proportions. Whenever this is the case, other factors being equal, and the determination is proceeded with, low results are obtained. The substitution of conc. ammonium hydroxide for the $2N$ sodium carbonate solution makes the appearance of the above precipitate far less frequent, without having any adverse effect on the results.

2. It was found unnecessary to wait for the solution to cool and the precipitate to settle before filtering. On the contrary, filtration of the warm solution is generally quicker and the subsequent washing more efficient. Lead thionalide tends to precipitate in a sticky form and excess thionalide presumably tends to clog the pores of the filterplate, greatly slowing down filtration. Filtering the solution while still hot minimizes this effect.

3. Similar considerations make it advisable to use low suction for filtration, in order to prevent, as far as possible, sucking the precipitate close to the filterplate.

4. Filtration through a filterstick of fine porosity is very slow. No loss is observed with a filterstick of medium porosity*, and this is used in all determinations.

5. The order of application of the washing solutions to the precipitate as given by BERG[11], *i.e.* water first and acetone-water mixture next, was reversed with excellent results. Washing this way proved quicker and more efficient; thionalide solubility in water being very low[13], the former method tends to cause its precipitation, clogging the filterpores and thus impeding filtration. The subsequent washing with acetone often fails to remove this thionalide quantitatively; it dissolves later in the acid solution mixture, causing high results.

For quantities of lead ranging from 1 to 10 mg, precipitated in a 10 ml beaker**, the following order and volumes of wash solutions are adequate:

a. Acetone-water (mixture 1:1):
2 × 2 ml
3 × 1 ml
b. Water:
2 × 2 ml.

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* The dimensions of this filterstick are the same as those of the filterstick of fine porosity.

** In order to achieve efficient washing with a minimum volume of wash liquids, it was found advisable to use the smallest beaker possible. Under the conditions described, a 10—20 ml beaker proved adequate.

6. Low results were generally obtained until the method of achieving the quantitative solution of the precipitate was perfected. It was obvious that sucking the acid mixture back and forth through the filterplate and the subsequent transfer of the solution to the Erlenmeyer flask constituted a cumbrous procedure, often leading to losses. This was remedied by dissolving the washed precipitate, in the beaker in which the lead had been precipitated, by the addition of 4-6 ml of the acid mixture (Reagent No. 10) and transferring the solution by suction through the filterstick into a 50 ml Erlenmeyer flask.

For quantities of lead ranging from 1 to 10 mg, it was found adequate to wash the filterstick and beaker as follows:

Acid mixture (Reagent No. 10):
1 × 2 ml
3 × 1 ml,
each time sucking through.

7. Under the conditions described in the *Tentative Procedure*, atmospheric oxidation, from the moment potassium iodide is added, causes the endpoint to be uncertain. This difficulty is completely eliminated by bubbling carbon dioxide through the solution to be titrated, beginning before the introduction of the potassium iodide and continuing throughout the titration. This also provides efficient stirring of the solution during titration.

8. The titrated solution is diluted with about 20 ml of bi-distilled water, before back-titration with sodium thiosulphate. This dilution was found adequate for obtaining a clear endpoint.

9. Under the above conditions, in experiments in which about 10 ml of the acid mixture were used, a blank equal to 0.01 ml of 0.01N potassium iodate-iodide solution was found. This was deducted in each of the subsequent experiments.

Taking all these factors into consideration, the following final procedure was evolved.

FINAL PROCEDURE FOR THE MICRO-VOLUMETRIC DETERMINATION OF LEAD IN SOLUTION WITH THIONALIDE

To the slightly acid solution of lead nitrate, (1-10 mg lead in 1-5 ml solution) in a 10-20 ml* Pyrex glass beaker, about 50 mg of sodium potassium tartrate are added and the solution stirred to dissolve the tartrate. 1 drop of phenolphthalein solution is introduced and 1-2 drops of conc. ammonium hydroxide added to neutralize the solution; approximately 100 mg of potassium cyanide are added. The volume of the solution is doubled by the addition of 2N sodium carbonate solution. The precipitation of lead thionalide is next effected by the addition of a freshly prepared solution of 40-50 mg of thionalide in 1-2 ml of acetone dropwise and with continuous stirring. The mixture is cautiously heated on an asbestos mat to boiling (caution-there is a tendency to squirting) and immediately filtered with low suction through a filterstick (medium porosity) (Fig. 1). Beaker and precipitate are washed with:

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* The size of the beaker depends on the quantity of the lead and the volume of the sample.

a. Acetone-water (mixture 1 : 1):
2 × 2 ml
3 × 1 ml.
b. Water:
2 × 2 ml.

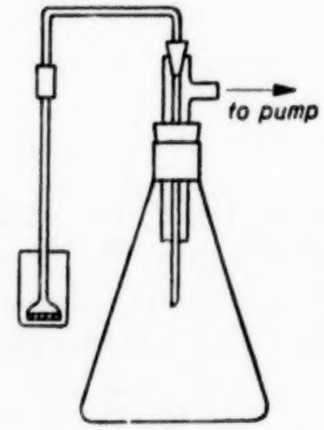

Fig. 1. Apparatus for filtration

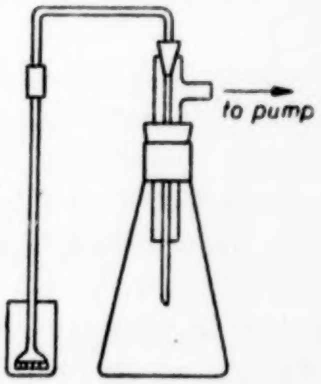

Fig. 2. Apparatus for filtration

Whenever the precipitate has been sucked too close to the filterplate, the plate is cautiously scraped with a glass stirring rod. Next the filterstick is detached from the suction system and the beaker, stirring rod and filterstick washed down with 4-6 ml of the acid mixture (Reagent No. 10). The precipitate is scraped off the filterplate and the larger particles squashed to effect complete decomposition of the lead thionalide. The filterstick is now connected again to the suction system and the solution of the thionalide sucked through it into a 50 ml Erlenmeyer flask (Fig. 2). Beaker and stick are then washed repeatedly with the acid mixture (Reagent No. 10), 1 × 2 ml, 3 × 1 ml, each time sucking the wash liquid through the stick into the Erlenmeyer flask. The Erlenmeyer flask is now detached from the suction system, a capillary tube leading to a Kipp apparatus is introduced into the solution and carbon dioxide (Reagent No. 11) bubbled through it.

Approximately 20 mg of potassium iodide are now added and standard potassium iodate-iodide solution introduced from a micro-burette, graduated to 0.01 ml*, until excess iodine is apparent from the light yellow colour of the liquid. (For samples containing 1-5 mg of lead, 0.01N potassium iodate-iodide solution is used; for 5-10 mg of lead, 0.02N solution). The mixture is now diluted with approximately twice its own volume of bi-distilled water, 1 ml 1% starch solution added and back-titrated with 0.01*N* sodium thiosulphate solution to the disappearance of the blue colour, using a similar micro-burette. For the quantities and reagents used above, it was found necessary to deduct a blank equal to 0.01 ml of 0.01*N* potassium iodate-iodide solution. 1 ml 0.01*N* potassium iodate-iodide solution —→ 1.036 mg lead.

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* The micro-burettes employed were Blue Line "Exax" burettes (U.S.A.), 5 ml capacity, with a graduation interval of 0.01 ml and a platinum alloy delivery tip, giving approximately 100 drops per ml.

The time required for 1 determination is approximately 45 minutes to 1 hour.

Remark

After the determination the filtersticks are cleaned by washing repeatedly first with warm conc. ammonium acetate solution and then with water. After about 30-40 experiments, the filtersticks usually show definite signs of being worn thin and must be discarded.

The experiments leading to the elaboration of the final procedure were all carried out on samples containing 3 mg of lead, this having been found most convenient. Once the method had been established, it was tested, on samples containing 1-10 mg of lead, with satisfactory results.

The results obtained are given in Table 1.

TABLE I

DETERMINATION OF LEAD IN LEAD NITRATE SOLUTION

Exp. No.	Pb present mg	KIO_3-KI solution added, ml		0.01*N* $Na_2S_2O_3$ solution used, ml	Pb found mg	Pb difference mg	Relative error %
		0.01*N*	0.02*N*				
1	1.000	1.00		0.025	1.000	—	—
2	1.000	1.00		0.03	0.995	—0.005	—0.5
3	2.000	2.00		0.06	1.999	—0.001	—0.05
4	2.000	2.00		0.065	1.994	—0.006	—0.3
5	4.000	4.00		0.14	3.989	—0.011	—0.3
6	4.000	4.00		0.135	3.994	—0.006	—0.15
7	6.000		3.00	0.21	5.988	—0.012	—0.2
8	6.000		3.00	0.22	5.978	—0.022	—0.4
9	8.000		4.00	0.29	7.977	—0.023	—0.3
10	8.000		4.00	0.26	8.008	+0.008	+0.1
11	10.000		5.00	0.35	9.987	—0.013	—0.1
12	10.000		5.00	0.37	9.966	—0.034	—0.3

Remark

In all of the above calculations a blank correction was applied equivalent to 0.01 ml of 0.01*N* potassium iodate- iodide solution. Obviously this blank must be determined, by experiment, according to the reagents used.

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Conclusion

As indicated by Table I, results are exact (maximum relative error ±0.5%).

Potassium cyanide and sodium potassium tartrate were added in varying amounts to samples before carrying out the determinations. No interference was detected, although up to 400 mg of each substance had been added.

PRELIMINARY EXPERIMENTS LEADING TO THE APPLICATION OF THE METHOD EVOLVED TO ALLOYS

As the elaboration of the micro-volumetric determination of lead had been attempted with a view to applying it to the determination of lead in tin-base and lead-base alloys, in which case the preliminary separation of lead from the remaining constituents of the alloy was mandatory, it was decided to examine — A: the possibility of separating the lead as lead sulphate, and B: subsequently dissolving it in ammonium acetate solution and determining it with thionalide in this medium.

A. As a first step, ammonium acetate was tested for interference in the established procedure. A series of determinations on 3 mg lead samples contained in 3 ml solution was carried out; to each sample, quantities of ammonium acetate ranging from 300 to 1000 mg were added.

The results obtained are given in Table II.

TABLE II

DETERMINATION OF LEAD IN SOLUTIONS CONTAINING VARYING AMOUNTS OF AMMONIUM ACETATE (REAGENT No. 17)

Exp. No.	Pb present mg	CH_3COONH_4 present mg	Pb found mg	Pb difference mg	Relative error %
1	3.000	300	3.016	+0.016	+0.5
2	3.000	500	3.080	+0.080	+2.7
3	3.000	700	3.102	+0.102	+3.4
4	3.000	1000	3.146	+0.146	+4.9

Conclusion

As indicated by Table II, results were high, increasing with increased ammonium acetate content.

DISCUSSION II

1. As shown by a rough pH determination, the addition of approximately 300 mg of ammonium acetate to the lead nitrate solution, containing all the reagents except the thionalide, lowers the pH of the solution by 1-1.5 pH units. Attempts to readjust the pH prior to the precipitation, by the addition of sodium hydroxide, gave no satisfactory results. On the other hand, the addition of up to 300 mg of sodium acetate instead of the ammonium acetate to the sample, did not interfere.

2. Seeing that the changed pH was not the cause of the unsatisfactory results, it was decided to try precipitating the lead with thionalide from the hot solution, *i.e.* heating the solution *before* adding the thionalide. This gave satisfactory results for determinations carried out on samples containing 3 mg of lead and 300 mg of ammonium acetate. Heating the solution, however, often caused the appearance of a white precipitate or turbidity, so that many determinations could not be completed. It was found best to heat the solution, containing all the ingredients up to and including the potassium cyanide, separately, and the $2N$ sodium carbonate solution separately, mix them quickly and add the thionalide solution.

B. Next, lead sulphate was precipitated from standard lead nitrate solution, by the addition of 0.15-0.3 ml of conc. sulphuric acid (caution) to 3 ml of the lead nitrate solution containing 3 mg of lead, evaporating to white fumes and diluting, after cooling, with 2 ml of water. (This was carried out in a 10 ml beaker). After settling, the precipitate was filtered through a filterstick (medium porosity) and washed with 3 × 1 ml of water, each time sucking the wash liquid through the filterstick. The filterstick was then detached from the suction system, the sides of the beaker and the filterstick carefully washed down with 0.75 ml of a 40% solution of ammonium acetate, the filterstick rotated gently until all the lead sulphate dissolved (very gentle heating may be applied) and finally the solution sucked through the stick into another 10 ml beaker (Fig. 3). The first beaker and stick were carefully washed with water, 3 × 1 ml, each time sucking the wash liquid through the stick. The solution of lead in the second beaker was then treated according to the procedure outlined above (see final procedure for the micro-volumetric determination of lead in solution with thionalide), except for the modifi-

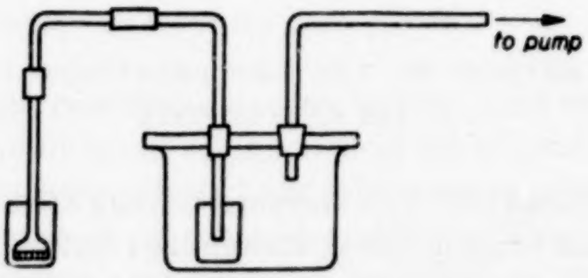

Fig. 3. Apparatus for filtration.

cation of heating the solution prior to the addition of the thionalide (see Discussion II, section 2).

The results obtained are given in Table III.

TABLE III

DETERMINATION OF 3 mg OF LEAD, AFTER PRECIPITATION AS LEAD SULPHATE AND ITS REDISSOLUTION IN 300 mg OF AMMONIUM ACETATE

Exp. No.	Pb present mg	CH_3COONH_4 present mg	Pb found mg	Pb difference mg	Relative error %
1	3.000	300	3.003	+0.003	+0.1
2	3.000	300	3.004	+0.004	+0.1
3	3.000	300	3.012	+0.012	+0.4
4	3.000	300	3.015	+0.015	+0.5

Conclusion

As indicated by Table III, results are exact (maximum relative error: ±0.5%).

Remark

For quantities of lead exceeding 3 mg, 300 mg of ammonium acetate were not always sufficient to effect complete solution of the lead sulphate precipitate. On the other hand, it was deemed unsatisfactory to introduce more ammonium acetate into the solution. 3 mg of lead was therefore chosen as the upper limit for determinations of this kind. The lower limit — 1 mg of lead — is set by the limit of the determination of lead in solution.

Having shown that lead may also be determined satisfactorily after precipitation as lead sulphate and redissolution with ammonium acetate, the determination of lead in tin-base and lead-base alloys was attempted.

APPLICATION OF THE METHOD TO THE DETERMINATION OF LEAD IN ALLOYS

I. TIN-BASE ALLOYS

The determination of lead in U.S.A. National Bureau of Standards Alloy No. 54c.

This alloy is a tin-base bearing metal, containing: 86.29% tin, 7.28% antimony, 1.99% lead, 4.30% copper, 0.033% iron, 0.028% bismuth, 0.012% nickel, 0.049% arsenic and 0.02% silver.

Tentative procedure

A quantity of alloy, containing approximately 3 mg of lead, was dissolved in conc. sulphuric acid, evaporated to white fumes and diluted with water; the lead sulphate was filtered, washed and determined as above. First results were high, due to incomplete removal of contaminating elements.

An attempt to scale down the A.S.T.M. hydrobromic acid method for the removal of antimony and tin[14] prior to the lead sulphate filtration was made. The results obtained are given in Table IV.

TABLE IV

DETERMINATION OF LEAD IN ALLOY NO. 54C AFTER REMOVAL OF ANTIMONY AND TIN ACCORDING TO THE A.S.T.M. HBr[14] METHOD

Exp. No.	Alloy 54c mg	Pb present mg	Pb found mg	Pb difference mg	Pb % theoretic	Pb % found	Difference %	Relative error %
1	150.000	2.985	2.981	—0.004	1.99	1.987	—0.003	—0.1
2	150.000	2.985	2.989	+0.004	1.99	1.993	+0.003	+0.1
3	150.000	2.985	2.982	—0.003	1.99	1.988	—0.002	—0.1

Conclusion

As indicated by Table IV, results were exact.

In spite of the exact results obtained by the hydrobromic acid method, it was deemed to be too cumbersome to be of practical value on the micro-scale.

It was decided to attempt to find the right conditions of solution, dilution and washing to give sufficiently exact results without recourse to the above separation. Those conditions have been established and are given below.

Final procedure recommended for tin-base alloys

A quantity of alloy, containing approximately 3 mg of lead, is introduced into a 30 ml beaker, 3 ml of conc. sulphuric acid added and heated cautiously until complete solution has been effected and white fumes appear. After cooling, 15 ml of alcohol-water (mixture 1 : 1) are added. After settling, the precipitate is filtered through a filterstick (medium porosity) and washed with sulphuric acid 10%, 3 × 2 ml, and alcohol-water (mixture 1 : 1), 3 × 2 ml. The filterstick is then detached from the suction system, the sides of the beaker and the filterstick carefully washed down with 0.75 ml of a 40% solution of ammonium acetate, the filterstick rotated gently until all of the lead sulphate dissolves (very gentle heating may be applied) and finally the solution sucked through the filterstick into another 10 ml beaker. The first beaker and stick are carefully washed with water, 3 × 1 ml, each time sucking the wash liquid through the stick. The solution of lead in the second beaker is then treated according to the procedure outlined under the final procedure for the micro-volumetric determination of lead in solution with thionalide, except for the modification of heating the solution prior to the addition of the thionalide (see Discussion II, section 2).

The time required for 1 determination is 2 hours approximately.

The results obtained are given in Table V.

TABLE V

DETERMINATION OF LEAD IN ALLOY NO. 54C

Exp. No.	Alloy 54c mg	Pb present mg	Pb found mg	Pb difference mg	Pb % theoretic	Pb % found	Difference %	Relative error %
1	150.000	2.985	2.988	+0.003	1.99	1.992	+0.002	+0.1
2	150.000	2.985	2.975	—0.010	1.99	1.983	—0.007	—0.3
3	150.000	2.985	2.970	—0.015	1.99	1.980	—0.010	—0.5
4	150.000	2.985	2.974	—0.011	1.99	1.983	—0.007	—0.3

Conclusion

As indicated by Table V, results were exact (maximum absolute difference was 0.01%, which is equivalent, in the case of this alloy, to a maximum relative error of 0.5%).

DISCUSSION III

1. The volume of sulphuric acid used for dissolving the alloy must be sufficiently large to keep all the tin sulphate formed in solution and also to minimize the formation of colloidal sulphur[15]. This effectively prevents bumping and simplifies the subsequent filtration.

2. Where dilution is made with water only, omitting the alcohol, results tend to be low.

3. The addition of 15 ml of alcohol-water (mixture 1 : 1) is necessary: (a)

to reduce the concentration of sulphuric acid to 10-15%, facilitating the solution of contaminating substances; (b) to reduce the solubility of lead sulphate (this is necessary in view of the large volume required according to (a)).

II LEAD-BASE ALLOYS

The determination of lead in U.S.A. National Bureau of Standards Alloy No. 53c.

This is a lead-base bearing metal, containing: 5.16% tin, 10.20% antimony, 0.214% copper, 0.0017% iron, 0.093% bismuth, 0.0023% nickel, 0.044% arsenic and lead (the rest).

Procedure recommended for lead-base alloys

A quantity of alloy, containing approximately 3 mg of lead, is introduced into a 10 ml beaker, 0.5 ml of conc. sulphuric acid added and heated cautiously until complete solution has been effected and white fumes appear. After cooling, 2 ml of water are added, the precipitate is allowed to settle and is then filtered through a filterstick (medium porosity), washed with sulphuric acid 10%, 3 × 1 ml, and alcohol-water (mixture 1 : 1), 3 × 1 ml. The filterstick is then detached from the suction system, the sides of the beaker and the stick carefully washed down with 0.75 ml of a 40% solution of ammonium acetate, the filterstick rotated gently until all of the lead sulphate dissolves (very gentle heating may be applied) and finally the solution sucked through the filterstick into another 10 ml beaker. The first beaker and stick are carefully washed with water, 3 × 1 ml, each time sucking the wash liquid through the stick. The solution of lead in the second beaker is then treated according to the procedure outlined under the final procedure for the micro-volumetric determination of lead in solution with thionalide, except for the modification of heating the solution prior to the addition of the thionalide (see Discussion II, section 2).

The time required for 1 determination: 2 hours approximately.

The results obtained are given in Table VI.

TABLE VI

DETERMINATION OF LEAD IN ALLOY NO. 53C

Exp. No.	Alloy 53c mg	Pb present mg	Pb found mg	Pb difference mg	Pb % theoretic	Pb % found	Difference %	Relative error %
1	3.235	2.726	2.720	—0.006	84.285	84.08	—0.20	—0.2
2	3.035	2.558	2.558	—	84.285	84.285	—	—
3	3.503	2.952	2.947	—0.005	84.285	84.13	—0.15	—0.2
4	3.532	2.977	2.990	+0.013	84.285	84.65	+0.37	+0.4

Conclusion

As indicated by Table VI, results were exact (maximum relative error ±0.4%).

APPLICATION OF THE METHOD TO ALLOYS WITH A LEAD CONTENT VARYING FROM 5% TO 72% OF LEAD

The above procedures were next applied to a series of alloys with a lead content varying from 5% to 72% of lead.

For alloys containing up to 20% of lead, the procedure described for alloy No. 54c was essentially used. The only modifications consisted of the use of a 20 ml beaker, instead of the 10 ml beaker, for alloys containing 5% to 20% of lead, and the proportionately smaller volumes of sulphuric acid used for the solution of the alloy, *e.g.*:

For alloys containing approx. 5% lead ---- 2 ml conc. sulphuric acid
,, ,, ,, ,, 10% ,, ---- 1.5 ,, ,, ,, ,,
,, ,, ,, ,, 20% ,, ---- 1 ,, ,, ,, ,,

The quantity of alloy taken for each determination was such as to contain approximately 3 mg of lead. The amount of alcohol-water (mixture 1 : 1) used for dilution also decreased in proportion to the amount of acid present, *e.g.*:

For alloys containing approx. 5% lead ----10 ml alcohol-water(1 : 1)
,, ,, ,, ,, 10% ,, ---- 8 ,, ,, ,,
,, ,, ,, ,, 20% ,, ---- 6 ,, ,, ,,

For alloys containing from 20% of lead and upwards, the method described for alloy No. 53c was applied.

Table VII contains the composition of the additional* alloys tested.

TABLE VII

Alloy No.	Pb %	Sn %	Sb %	Cu %
1	5.16	85.7	7.16	2.0
2	9.7	78.2	8.3	3.8
3	20.1		the rest	
4	28.9		the rest	
5	46.0		the rest	
6	72.5	9.4	18.04	

The results obtained in determinations carried out on the alloys enumerated in Table VII, are given in Table VIII.

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* Results of the determination of lead in pure lead metal, in an alloy containing 1.99% lead (No. 54c) and in an alloy containing 84.285% lead (No. 53c) are given in Tables I, III, V and VI respectively.

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TABLE VIII

DETERMINATION OF LEAD IN ALLOYS WITH A VARYING LEAD CONTENT (5%—72%)

Exp. No.	Alloy No.	Alloy mg	Pb present mg	Pb found mg	Pb difference mg	Pb % theoretic	Pb % found	Difference %	Relative error %
1	1	61.240	3.160	3.156	—0.004	5.16	5.15	—0.01	—0.2
2	1	62.400	3.220	3.214	—0.006	5.16	5.15	—0.01	—0.2
3	2	32.020	3.106	3.112	+0.006	9.7	9.72	+0.02	+0.2
4	2	30.022	2.912	2.912	—	9.7	9.70	—	—
5	3	15.015	3.018	3.009	—0.009	20.1	20.04	—0.06	—0.3
6	3	14.041	2.822	2.814	—0.008	20.1	20.04	—0.06	—0.3
7	4	9.820	2.838	2.832	—0.006	28.9	28.84	—0.06	—0.2
8	4	10.982	3.174	3.183	+0.009	28.9	28.98	+0.08	+0.3
9	5	6.052	2.784	2.792	+0.008	46.0	46.13	+0.13	+0.3
10	5	5.620	2.585	2.583	—0.002	46.0	45.96	—0.04	—0.1
11	6	5.341	3.872	3.872	—	72.5	72.5	—	—
12	6	4.555	3.302	3.299	—0.003	72.5	72.42	—0.08	—0.1

Conclusion

As indicated by Table VIII, results were exact (maximum relative error ±0.3%).

APPLICATION OF THE METHOD TO ALLOYS HAVING AN APPROX. COPPER CONTENT OF 10%

Most of the alloys examined being low in copper content, it was decided to add cupric sulphate solution (30 g $CuSO_4.5H_2O$ per litre) to samples of these alloys, in order to test the applicability of the method to samples having a higher copper content. Enough cupric sulphate solution was added to bring the copper content to about 10%. The usual procedures were adhered to.

The results obtained are given in Table IX.

TABLE IX

DETERMINATION OF LEAD IN ALLOYS WITH THE ADDITION OF CUPRIC SULPHATE TO A COPPER CONTENT OF APPROX. 10%

Exp. No.	Alloy No.	Alloy mg	Pb present mg	Pb found mg	Pb difference mg	Pb % theoretic	Pb % found	Difference %	Relative error %
1	54c	150.000	2.985	3.000	+0.015	1.99	2.00	+0.01	+0.5
2	54c	150.000	2.985	2.976	—0.009	1.99	1.983	—0.007	—0.3
3	5	6.003	2.761	2.766	+0.005	46.0	46.08	+0.08	+0.2
4	5	6.306	2.901	2.893	—0.008	46.0	45.88	—0.12	—0.3
5	53c	3.403	2.868	2.863	—0.005	84.285	84.13	—0.15	—0.2
6	53c	3.030	2.554	2.559	+0.005	84.285	84.46	+0.16	+0.2

Conclusion

As indicated by Table IX, results were exact (maximum relative error: ±0.5%).

SUMMARY

The authors have elaborated an exact micro-volumetric method for the determination of lead with thionalide. The method has been successfully applied to the determination of lead in tin-base and lead-base alloys, following the isolation of lead as lead sulphate and its redissolution in ammonium acetate.

RÉSUMÉ

Les auteurs ont élaboré une micro-méthode volumétrique exacte pour la détermination du plomb au moyen de thionalide. Ils ont appliqué avec succès la méthode établie pour la détermination du plomb dans les alliages à base d'étain et de plomb, après l'avoir isolé à l'état de sulfate de plomb et dissous dans une solution d'acétate d'ammonium.

ZUSAMMENFASSUNG

Die Verfasser haben eine exakte Mikro-volumetrische Methode zur Bestimmung des Bleis mit Thionalid ausgearbeitet. Die Methode wurde erfolgreich zur Bestimmung des Bleis in Blei- und Zinn-Legierungen verwandt, nachdem das Blei als Bleisulfat isoliert und in Ammoniumacetat gelöst wurde.

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THE SEMI-MICRO DETERMINATION OF FLUORINE, CHLORINE, AND NITROGEN IN ORGANIC COMPOUNDS

by

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The simultaneous determination of fluorine and chlorine in organic compounds by fusion with sodium in a nickel bomb, followed by determination of the fluoride and chloride ions by titration with thorium nitrate and silver nitrate respectively, is well known and has been described by MILLER, HUNT AND MCBEE[1]; and MUSGRAVE, SMITH AND TATLOW[2]. It has been shown by ELLIS AND MUSGRAVE[3] and by BELCHER, CALDAS, CLARK AND MACDONALD[4] that cyanide ion must be removed before an accurate determination of fluoride ion is possible but, as far as we know, no other attempts have been made to determine fluorine, chlorine, and nitrogen simultaneously in organic compounds via the fluoride, chloride, and cyanide ions produced in the solution from the one sodium fusion. We now find that it is possible to carry out such determinations only if the organic compound does not contain any oxygen because, when oxygen is present, a considerable proportion of the organic nitrogen is converted to cyanate ion which then hydrolyses to carbonate.

In the determination of fluorine, the cyanide ion was precipitated by adding excess silver nitrate and then removing the excess with sodium chloride solution as described by ELLIS AND MUSGRAVE[3]. BELCHER *et al*[4]. object to this method on the grounds that the precipitate is difficult to filter and wash, but their objection was overcome to some extent by making up the solution to a standard volume, filtering into dry apparatus, and then taking an aliquot of filtrate. This avoided washing the precipitate, a process which invariably results in colloidal silver cyanide passing through the filter. There is no doubt that some silver cyanide passed through but, on the semi-micro scale, this does not affect the results. The fluoride was then titrated in the usual way.

The problem now resolved itself into the determination of chloride and cyanide in the presence of each other, since the presence of fluoride ion does not interfere with the determination of either, and the best approach seemed to be (a) by a method reported on by GRAHAM[5] involving the removal of cyanide by the addition of formaldehyde followed by determination of the chloride by silver nitrate titration, and then (b) determination of the cyanide by the DENIGES[6] modification.

As an alternative to either (a) or (b), total cyanide and chloride could be determined by adding excess silver nitrate and back-titrating.

When using synthetic solutions containing semi-micro amounts of chloride, fluoride, and cyanide ions the Volhard method did not give a sufficiently sharp end-point. Phenosafranine gave no end-point, presumably because of reaction with the excess formaldehyde. Dichloro-R-fluorescein gave good results, but when applied to fusion solutions obtained from the bomb this was not so, and it was found that the only reliable method for both synthetic and test solutions was to add an excess of silver nitrate solution after destroying the cyanide, filter, wash, and titrate the excess with bromide solution using Rhodamine BS as indicator. If the silver chloride is well coagulated instead of being filtered, the results are still satisfactory. Rhodamine 6G has been used previously by FAJANS AND WOLFF[7] for sodium bromide-silver nitrate titrations but was not available; Rhodamine BS was chosen since it also has no free amino groups which could react with the excess formaldehyde.

The cyanide determination by the Deniges method gave excellent results when used with synthetic solutions containing chloride, fluoride and cyanide, but with solutions from the bomb the results were, at first, much too low, being often little more than half the theoretical value. The greatest error was found to be due to the oxygen in the organic compound causing the production of cyanate ion as well as cyanide. This cyanate was then hydrolysed to carbonate, which showed itself in a vigorous evolution of carbon dioxide on acidification of the fusion solution with dilute nitric acid. Another error resulted from the fusion of liquids which were sealed in glass capsules. The explosion of the capsule threw

TABLE I

Compound (g)		% Cl Calc.	% Cl Found	% N Calc.	% N Found	
o-chloronitrobenzene	(0.1099)	22.54	22.4	8.89	4.3	Solid weighed directly into bomb. Error due to production of cyanate
,,	(0.1355)	22.54	22.5	8.89	5.0	
,,	(0.1910)	22.54	22.5	8.89	4.4	
Aniline	(0.0906)			15.05	14.0	Error due to fusion in glass capsule.
Pyridine	(0.0798)			17.72	16.6	
Aniline hydrobromide	(0.1035)			8.05	8.14	Solid, weighed directly into bomb. No Ni foil over Cu washer.
Aniline	(0.1126)			15.05	15.1	Liquids, weighed in Ni capsule-Ni foil covering Cu washer.
				15.05	15.2	
Pyridine	(0.0938)			17.72	17.8	
		% F Calc.	% F Found			
Monofluoropyridine	(0.0894)	19.59	19.3	14.44	14.1	

the organic compound and sodium against the copper washer covering the top of the bomb and reaction then occurred between the sodium cyanide and the copper to give a complex cyanide Na_3 [Cu(CN)$_4$]. This would then react with the silver nitrate to give Ag_3[Cu(CN)$_4$] which requires less silver ion than would the cyanide when present as free cyanide ion. The presence of such a complex was indicated by the formation of a yellow-brown precipitate in addition to the white silver cyanide in these cases. When thin nickel foil was used over the copper washer, and when the organic compounds were weighed in nickel capsules the error was eliminated. Results illustrating the points mentioned above are given in Table I.

Attempts (the results of which are given in Table II) were also made, by omitting the addition of formaldehyde, to estimate chloride and cyanide together by the method used for the chloride estimation. It was found that back titration without filtration gave very poor results, and simple filtration and washing were equally unsatisfactory, in each case because of the presence of colloidal silver cyanide. Finally, good results were obtained on synthetic solutions by making up to a standard volume after precipitating, filtering through a thick wad of filter papers (six No. 50 papers), and taking an aliquot of the filtrate without washing the precipitate. However, when applied to fusion solutions the combined nitrogen

TABLE II

Compound (g)	% F Calc.	% F Found	% Cl Calc.	% Cl Found	% N Calc.	% N Found	
o-chloronitrobenzene							
(0.1009)			22.5	22.4	8.9	5.8	Errors due mainly to cyanate production
,, (0.1854)			22.5	22.4	8.9	5.2	
p-nitroaniline							
(0.1364)					20.3	12.7	
2-chloro-5-trifluoromethyl-acetanilide $C_{11}H_9O_2NClF_3$							
(0.1841)	20.4	20.1	12.7	12.6	5.0	4.4	
,, (0.1937)					5.0	4.3	
Aniline							Liquids weighed in glass capsules. Error due mainly to Cu complex formation
(0.0906)					15.05	12.5	
(0.1242)					15.05	12.6	
Pyridine							
(0.0798)					17.72	15.5	
Aniline							Liquids weighed in Ni capsules and with Ni foil over Cu washer
(0.1126)					15.05	13.2	
Pyridine							
(0.0938)					17.72	15.9	
			% Br Calc.	% Br Found			
Aniline hydrobromide							Solid weighed directly into bomb Cu washer without Ni foil.
(0.1035)			46.0	45.8	8.05	8.00	

plus chlorine result was always about 1.0% low even when there was no oxygen in the compound and precautions were taken to prevent the formation of copper complexes. Only one good result, with aniline hydrobromide, was ever obtained and this cannot be explained. The error could not be due to the formation of a nickel complex, since such a complex would have to be stable in the presence of silver ion, and FLASCHKA AND HUDITZ[8] have shown that the ordinary nickel cyanide complex is decomposed on addition of silver ions

$$2\ Ag^{+2} + [Ni(CN)_4]^{-2} \rightarrow 2\ [Ag(CN)_2]^- + Ni^{+2}$$

EXPERIMENTAL METHODS

Weigh a sample of organic compound, containing about 10 mg of each of the elements to be determined, using a nickel capsule if the compound is liquid. Fuse with sodium in a nickel bomb, using either a copper or nickel washer, at a temperature of 600-700°C. When the bomb has cooled, destroy the excess sodium with the minimum amount of alcohol and wash into a beaker. Warm the mixture to about 50° for two minutes (longer heating or higher temperature results in loss of HCN) to ensure complete extraction, cool, filter, and make up filtrate and washings to 150 ml.

Fluoride determination

As described by MUSGRAVE, SMITH AND TATLOW[2], or by BELCHER, CALDAS, CLARK AND MACDONALD[4].

Chloride determination

Take an aliquot (50 ml) of the fusion solution, treat with $0.1M$ aqueous formaldehyde (10 ml) and neutralize with $2N$ HNO_3 using phenolphthalein as indicator. Now add concentrated HNO_3 (2 ml) and an excess of $0.01N$ $AgNO_3$, filter off the AgCl using a Whatman No. 50 filter paper, and wash the precipitate several times with distilled water. Titrate the filtrate and washings with $0.01N$ KBr using six drops of Rhodamine BS (0.050 aqueous solution) as indicator.

Cyanide determination (*Deniges method*)

Treat an aliquot (25 ml) of the test solution with $6N$ ammonia solution (7 ml), $0.1N$ KI (2 drops), and titrate with silver nitrate to a permanent turbidity.

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SUMMARY

The organic compounds are fused with sodium in a nickel bomb in the usual way and the fluoride, chloride, and cyanide ions produced are determined. The method cannot be used to determine nitrogen in organic compounds containing oxygen since, in such cases, some of the nitrogen is converted to cyanate ion.

RÉSUMÉ

Les composés organiques sont fondus avec du sodium dans une bombe de nickel, par le procédé habituel; on effectue ensuite le dosage des ions fluorhydrique, chlorhydrique et cyanhydrique formés. Cette méthode ne peut pas être utilisée pour le dosage de l'azote dans les substances organiques renfermant de l'oxygène, une partie de l'azote serait transformée en ion cyanique.

ZUSAMMENFASSUNG

Die organischen Stoffe werden nach dem bekannten Verfahren in einer Bombe aus Nickel mit Natrium zusammen geschmolzen. Anschliessend führt man die Bestimmung der gebildeten Fluorid-, Chlorid- und Cyanidionen aus. Diese Methode kann nicht verwendet werden für die Bestimmung von Stickstoff in organischen Substanzen welche Sauerstoff enthalten da ein gewisser Teil des Stickstoffes zur Bildung von Cyanationen beiträgt.

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THE DETERMINATION OF NICKEL WITH DIMETHYLGLYOXIME IN THE PRESENCE OF IRON AND COBALT*

by

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The gravimetric determination of nickel by precipitation with dimethylglyoxime, as first described by BRUNCK[1,2], has been studied extensively. The method is very satisfactory for the separation of nickel from a large number of foreign ions, including iron and cobalt. The cobalt complex is soluble and therefore does not interfere, and the precipitation of iron hydroxide is prevented by the addition of tartaric acid. However, if iron and cobalt are present together, a voluminous, amorphous precipitate is produced, even in the presence of tartaric acid[3,4]. According to WEELDENBURG[4] this contaminant has the formula, $FeCoC_{12}H_{19}N_6O_6$, but CHIRNSIDE, CLULEY AND PROFITT report that the composition is variable[5]. The precipitate is difficult to filter and the contaminant cannot be removed by washing. This iron-cobalt-dimethylglyoxime contaminant is formed only by ferric iron, and methods have been devised to prevent its formation by reduction of the iron to the divalent state[3,4,5,6].

In the present paper it is shown that quantitative precipitation of nickel with dimethylglyoxime in the presence of ferric iron and cobalt can be made in the presence of N,N-dihydroxyethylglycine. In this investigation ethylenediaminetetraacetic acid, and ammoniatriacetic acid were also studied and found to be unsatisfactory.

METHOD

Reagents

Iron solution. A solution of reagent grade ferric nitrate was used.

Cobalt solution. Reagent grade cobaltous chloride was used.

Nickel solution. Reagent grade nickel carbonate was dissolved in dilute hydrochloric acid. The solution was standardized by titration with cyanide, and checked by precipitation with dimethylglyoxime.

Ethylenediaminetetraacetic acid. The reagent grade of the disodium salt, as

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provided by the Bersworth Chemical Company, Framingham, Massachusetts, was used without further purification.

Ammoniatriacetic acid. This reagent was purchased from Eastman Kodak Company, Rochester, New York.

N,N-Dihydroxyethylglycine. A 47% solution of this reagent as provided by the Mac Chemical Company, Knoxville, Tennessee, was used for the nickel determinations. A small amount of the pure acid, obtained from Bersworth Chemical Company, was used in the preliminary tests to determine its effect on iron and nickel.

Dimethylglyoxime solution. A 1% solution in ethanol was used.

Experimental

To determine the effect of the chelating agent on the metal ion, an excess of the agent was added to an acidic solution of the metal ion, and the solution was made slightly basic with ammonium hydroxide. Ethylenediaminetetraacetic acid and ammoniatriacetic acid both form soluble chelates with iron, cobalt, and nickel, and prevent the precipitation of ferric hydroxide under the stated conditions, but their chelates with nickel are strong enough to prevent the precipitation of the latter with dimethylglyoxime. It was found that the addition of an excess of calcium chloride solution to either the nickel-ammoniatriacetic acid chelate or to the nickel-ethylenediaminetetraacetic acid chelate will allow the nickel to be quantitatively precipitated by dimethylglyoxime. However, this excess of calcium ion will also allow ferric hydroxide to be precipitated from the slightly ammoniacal solution of iron in the presence of either of these chelating agents. Solutions of strontium, barium, and magnesium ions give results identical to those obtained with calcium. Thus, the interference of iron in the precipitation of nickel with dimethylglyoxime cannot be prevented by ammoniatriacetic acid or by ethylenediaminetetraacetic acid.

N,N-Dihydroxyethylglycine prevented the precipitation of ferric hydroxide, not only in the slightly ammoniacal solution which is most favorable for the precipitation of nickel with dimethylglyoxime, but even at a pH as high as 11 or above. This reagent chelates nickel, but the chelate is not strong enough to prevent the quantitative precipitation of nickel by dimethylglyoxime unless a very large excess (50 g or more) of the chelating agent is present. Even if enough N,N-dihydroxyethylglycine is present to chelate the nickel somewhat, the addition of an excess of zinc chloride solution will allow the quantitative precipitation of the nickel. The solution of zinc chloride has no effect on the iron chelate of N,N-dihydroxyethylglycine.

In order to learn whether N,N-dihydroxyethylglycine would prevent the formation of the iron-cobalt-dimethylglyoxime compound, a solution containing iron, cobalt, and nickel was treated with twice the amount of chelating agent

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necessary to chelate the iron present; the solution was heated to boiling, dimethylglyoxime solution was added, the solution was made slightly ammoniacal, and allowed to stand until cool (at least one hour). The solution was filtered through a weighed Gooch crucible and washed with cold water. The filtrate was tested for completeness of precipitation by the addition of more dimethylglyoxime solution and zinc chloride solution. The precipitate was dried to constant weight at 110°. The weight of nickel was found by multiplying the weight of the precipitate by the factor 0.2032.

RESULTS

The results of the precipitation of nickel with dimethylglyoxime in the presence of both iron and cobalt, using N,N-dihydroxyethylglycine to prevent the formation of the interfering iron-cobalt-dimethylglyoxime precipitate, are given in Table I. The method is very simple, requiring only the addition of the chelating agent before following the regular procedure for the determination of nickel with dimethylglyoxime. The results are accurate, and no trouble is encountered in filtration.

TABLE I

PRECIPITATION OF NICKEL WITH DIMETHYLGLYOXIME IN THE PRESENCE OF IRON AND COBALT

Nickel taken (mg)	Cobalt (mg)	Iron (mg)	N,N-Dihydroxyethylglycine (grams)	Nickel found (mg)
67.5	0.00	82.5	1	67.2
67.5	0.00	825.0	10	67.5
67.5	14.7	206.3	2.5	67.4
67.5	14.7	8.3	1	67.5
67.5	7.4	8.3	1	67.4
67.5	7.4	82.5	2	67.5
67.5	7.4	82.5	2	67.4
67.5	14.7	82.5	1.5	67.7
67.5	14.7	247.5	4.0	67.6
67.5	7.4	82.5	1.5	67.3
67.5	7.4	825.0	10	67.1
33.8	7.4	206.3	3.5	33.7
33.8	7.4	412.5	7	33.9
33.8	7.4	825.0	12.5	33.7
33.8	14.7	412.5	7.5	33.8

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SUMMARY

A method for the determination of nickel in the presence of both ferric iron and cobalt is presented. The nickel is precipitated directly with dimethylglyoxime, without the prior reduction of the iron. The interference of the iron and cobalt is eliminated by the addition of N,N-dihydroxyethylglycine, which chelates the iron and prevents the formation of the iron-cobalt-dimethylglyoxime contaminant.

RÉSUMÉ

Une méthode de dosage du nickel, en présence de fer(III) et de cobalt est proposée. Le nickel est précipité directement par la diméthylglyoxime, sans réduction préalable du fer. La perturbation du fer et du cobalt est éliminée par addition de N,N-dihydroxyéthylglycine, formant un chélate avec le fer et empêchant une coprécipitation de fer — cobalt-diméthylglyoxime.

ZUSAMMENFASSUNG

Es wird eine Methode für die Bestimmung von Nickel in Gegenwart von Eisen(III) und von Kobalt vorgeschlagen. Das Nickel wird direkt niedergeschlagen mit Dimethylglyoxime, ohne vorhergehende Reduktion des Eisens. Der störende Einfluss des Eisens und des Kobalts wird vermieden durch Zugabe von N,N-Dihydroxyethylglycin, welches mit dem Eisen ein Chelat bildet und so eine Mitausfällung von Eisen-Kobalt-dimethylglyoxime verhindert.

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DETERMINATION OF THORIUM WITH ORGANIC REAGENTS: USES OF SOME ARYL FATTY ACIDS

by

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INTRODUCTION

During our investigation on the thorium-precipitating action of a large number of organic acids [1-3] and their derivatives, it has been found that some aryl fatty acids produce voluminous precipitate with thorium. The present paper deals with the determination of thorium and its separation from artificial mixtures of thorium-cerium, thorium-cerium-lanthanum and from monazite sand and other elements, by phenylacetic-, phenylpropionic- and 1-naphthylacetic acids, under different conditions. The principal advantage in using these reagents lies in the separation they afford of thorium from the rare earths. No mention is found in the literature regarding the use of the acids of this series for the determination of thorium.

EXPERIMENTAL

Reagents and chemicals

Phenylacetic acid and 1-naphthylacetic acid (B.D.H. reagent grade) were purified by recrystallization from hot water. Phenylpropionic acid was prepared by the reduction of cinnamic acid as follows[4]:

20 g of cinnamic acid were stirred in 200 ml water contained in a beaker. A slight excess of dilute alkali was added and then 400 g of 2.5 per cent. sodium amalgam was added gradually in small pieces. When the reduction was complete, the solution was decanted from the mercury and acidified with hydrochloric acid. β-Phenylpropionic acid was precipitated as an oil, which soon solidified. It was then purified by recrystallization from hot water (m.p. 470° C). Stock solutions of pure reagent grade (Merck) thorium, cerium and lanthanum nitrates were prepared and the earth contents were determined as usual by the oxalate method.

Solutions of other metals like calcium, barium, zinc etc., were prepared by dissolving the A.R. quality nitrates or sulphates in water, as the case may be, and were determined by standard methods.

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Analytical procedures

Determination of thorium

A solution containing 0.001 to 0.1724 g of thorium oxide (made neutral to Congo red), was diluted to 40 ml and heated to boiling. A hot 1% solution of aryl fatty acid was then added. A white voluminous precipitate appeared immediately with phenylacetic acid, which soon coagulated and collected into a coherent mass towards the centre of the beaker. In the case of the other two acids, namely phenylpropionic acid and 1-naphthylacetic acid, a milkiness appeared first. On digesting for 10 minutes at the boiling temperature and stirring, the precipitate of phenylpropionate coagulated into flocks, but that with 1-naphthylacetic acid neither coagulated nor became granular even on digestion for 30 minutes. This milky suspension on filtering passed through the filter paper. On adding about 5 ml of 10% ammonium acetate solution, the milkiness of both the solutions cleared out at once owing to the formation of thorium salts of phenylpropionic- and naphthylacetic acids, and the precipitate assumed a granular form, which settled within two minutes. The precipitate was filtered while hot on a No. 41 Whatman filter paper and washed first with a 0.1% solution of the reagent containing 0.5% ammonium acetate and then five or six times with hot water. The paper and contents were dried and ignited to thorium oxide in a platinum crucible to constant weight. Tables I, II and III compare the results obtained with solutions of thorium nitrate using phenylacetic-, phenylpropionic- and 1-naphthylacetic acids.

TABLE I

DETERMINATIONS OF VARYING AMOUNTS OF THORIUM USING PHENYLACETIC ACID

Expt. No.	ThO_2 taken (Oxalate method)	ThO_2 found	Diff.
1	0.0862 g	0.0863 g	+ 0.0001 g
2	0.0755	0.0755	± 0.0000
3	0.0647	0.0648	± 0.0001
4	0.0431	0.0432	+ 0.0001
5	0.0216	0.0215	— 0.0001
6	0.0108	0.0108	± 0.0000
7	0.0054	0.0053	— 0.0001
8	0.0027	0.0026	— 0.0001
9	0.0014	0.0012	— 0.0002
10	0.0004	0.0002	— 0.0002

TABLE II

DETERMINATIONS OF VARYING AMOUNTS OF THORIUM USING PHENYLPROPIONIC ACID

Expt. No.	ThO_2 taken (Oxalate method)	ThO_2 found	Diff.
1	0.0862 g	0.0862 g	± 0.0000 g
2	0.0755	0.0756	+ 0.0001
3	0.0647	0.0645	— 0.0002
4	0.0431	0.0430	— 0.0001
5	0.0216	0.0217	+ 0.0001
6	0.0108	0.0105	— 0.0003
7	0.0054	0.0049	— 0.0005
8	0.0027	0.0012	— 0.0015
9	0.0014	..	..
10	0.0004	..	..

TABLE III

DETERMINATIONS OF VARYING AMOUNTS OF THORIUM USING 1-NAPHTHYLACETIC ACID

Expt. No.	ThO_2 taken (Oxalate method)	ThO_2 found	Diff.
1	0.0862 g	0.0861 g	— 0.0001 g
2	0.0755	0.0754	— 0.0001
3	0.0647	0.0645	— 0.0002
4	0.0431	0.0429	— 0.0002
5	0.0216	0.0213	— 0.0003
6	0.0108	0.0102	— 0.0006
7	0.0054	0.0044	— 0.0010
8	0.0027	0.0010	— 0.0017
9	0.0014	...	...
10	0.0004	...	...

Effect of hydrogen ion concentration upon precipitation

In order to find out the range of acid concentration suitable for effective precipitation, precipitations were carried out by the aryl fatty acids by following the procedure already described, except that pH of the final solution was varied.

The pH was adjusted by the addition of 0.1*N* HNO_3 or very dilute ammonia as the case may be, to the thorium solution. The precipitates were similarly washed and ignited to the oxide. The results are entered in the Table IV below:

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TABLE IV

ESTIMATION OF THORIUM AT DIFFERENT pH VALUES OF THE SOLUTION

ThO_2 taken = 0.0431 g
Total volume of the solution = 75 ml

Expt. No.	pH of the final solution	..... ThO_2 obtained by					
		Phenylacetic acid	Diff.	Phenylpropionic acid	Diff.	1-Naphthyl acid	Diff.
1	1.4	0.0331 g	— 10.0 mg	—	—	—	—
2	1.8	0.0339	— 9.2	—	—	—	—
3	2.0	0.0368	— 6.3	0.0329 g	— 10.2 mg	—	—
4	2.2	0.0399	— 3.2	0.0379	— 5.2	0.0359 g	— 7.2 mg
5	2.4	0.0419	— 1.2	0.0389	— 4.2	0.0379	— 5.2
6	2.8	0.0428	— 0.3	0.0403	— 2.8	0.0365	— 6.6
7	3.2	0.0429	— 0.2	0.0418	— 1.1	0.0411	— 2.0
8	3.6	0.0429	— 0.2	0.0428	— 0.3	0.0419	— 1.2
9	4.0	0.0430	— 0.1	0.0432	+ 0.1	0.0427	— 0.4
10	4.4	0.0432	+ 0.1	0.0431	+ 0.0	0.0429	— 0.2
11	4.6	0.0432	+ 0.1	0.0430	— 0.1	0.0431	± 0.0
12	4.8	0.0431	± 0.0	0.0432	+ 0.1	0.0432	+ 0.1
13	5.0	0.0432	+ 0.1	0.0433	+ 0.2	0.0432	+ 0.1
14	5.2	0.0433	+ 0.2	0.0433	+ 0.2	0.0432	+ 0.1

TABLE V

SEPARATION OF THORIUM FROM CERITE EARTHS

Expt. No.	ThO_2 taken	CeO_2 added	La_2O_3 added	Approx. ratio of thoria: cerite earths	ThO_2 found	
					Single pptn.	Double pptn.
			A. Phenylacetic acid			
1	0.0022 g	0.0172 g	—	1 : 8	0.0021 g	—
2	0.0022	0.0172	0.0120	1 : 14	0.0022	—
3	0.0044	0.0344	0.0360	1 : 16	0.0045	—
4	0.0044	0.0688	0.0360	1 : 24	0.0049	—
5	0.0044	0.0688	0.0480	1 : 26	—	0.0045 g
6	0.0044	0.0860	0.0480	1 : 30	—	0.0045
7	0.0044	0.0860	0.0840	1 : 39	—	0.0047
8	0.0044	0.1204	0.0840	1 : 46	—	0.0050
			B. Phenylpropionic acid			
1	0.0022	0.0172	—	1 : 8	0.0023	—
2	0.0022	0.0172	0.0060	1 : 10	0.0026	—
3	0.0022	0.0172	0.0120	1 : 14	. .	0.0024 g
4	0.0044	0.0344	0.0360	1 : 16	. .	0.0048
5	0.0044	0.0688	0.0360	1 : 24	. .	0.0052

TABLE V *(continued)*

Expt. No.	ThO_2 taken	CeO_2 added	La_2O_3 added	Approx. ratio of thoria: cerite earths	ThO_2 found Single pptn.	ThO_2 found Double pptn.
C. 1-Naphthylacetic acid						
1	0.0044	0.0172	. .	1 : 4	0.0043	—
2	0.0044	0.0172	0.0120	1 : 6	0.0043	—
3	0.0022	0.0172	. .	1 : 8	0.0027	—
4	0.0044	0.0172	0.0120	1 : 14	. .	—
5	0.0044	0.0344	0.0360	1 : 16	. .	0.0051

Separation of thorium from artificial mixtures of thorium-cerium and thorium-cerium-lanthanum present in solutions

After considerable experimentation, it was seen that thorium could be completely separated from the cerite earths, by phenylacetic acid between pH 3.2 and 5.2, by phenylpropionic acid between pH 4 and 5 and by naphthylacetic acid between pH 4.2 to 5. Different quantities of thorium, cerium and lanthanum nitrate solutions, were mixed together, and the mixture was brought to the definite pH range, suitable for the particular reagent to be used. Precipitation of thorium was done as before, the precipitate was washed thoroughly and ignited to the oxide as usual. Beyond a certain ratio of thoria — rare earth oxide in the mixture, we had to take recourse to double precipitation to avoid contamination. This is illustrated by the data given in Table V.

Determination of thorium in presence of foreign ions

Thorium can be be separated from a number of metals, such as calcium, barium, strontium, magnesium, manganese, aluminium, titanium etc. from a mixture of thorium and their salts with the help of aryl fatty acids. The pH range from 4.4 to 4.8 was found suitable for all of them. Only cobalt, nickel and manganese required double precipitation, even if present in relatively small quantities. Iron and zirconium interfered and hence thorium could not be separated from its mixture with them. A large quantity of uranium may be separated from thorium by double precipitation. The mean of three determinations, in each case, has been reported in Tables VI and VII.

TABLE VI

SEPARATION OF THORIUM FROM VARIOUS METALS

ThO_2 present = 0.0647 g

Metal oxide added	Amounts in grams	...... ThO_2 obtained by		
		Phenylacetic acid	Phenylpropionic acid	Naphthylacetic acid
BaO	0.2130	0.0643 g	0.0643 g	0.0642 g
CaO	0.1263	0.0642	0.0649	0.0641
SrO	0.2531	0.0644	0.0643	0.0642
ZnO	0.3106	0.0645	0.0648	0.0649
Al_2O_3	0.3213	0.0649	0.0650	0.0652
* Cr_2O_3	0.2012	0.0649	0.0652	0.0654
* NiO	0.2160	0.0650	0.0652	0.0653
* CoO	0.1232	0.0651	0.0654	0.0656
* MnO	0.1631	0.0650	0.0652	0.0653
TiO_2	0.3262	0.0648	0.0650	0.0652

TABLE VII

SEPARATION OF THORIUM FROM URANIUM

ThO_2 taken = 0.0044 g

Expt. No.	Amount of U_3O_8 added in g	...... ThO_2 obtained by			Ratio of ThO_2 U_3O_8
		Ph-acetic acid	Ph-propionic acid	Naphthyl-acetic acid	
* 1	0.0225	0.0046 g	0.0048 g	0.0050 g	(1 : 5)
* 2	0.0900	0.0050	0.0056	0.0057	(1 : 20)
* 3	0.2250	0.0052	0.0062	0.0071	(1 : 51)
* 4	0.2475	0.0058	. .	. .	(1 : 56)

* Indicates double precipitation.

Composition of thorium salts of aryl fatty acids

Thorium salts were prepared following the same procedure described before, except that a previously weighed glass sintered crucible replaced the filter paper and the filtration and the washing were carried out with the aid of suction. The precipitate was washed with hot water several times and then with hot 90% alcohol to remove the excess of the aryl fatty acids. The salts were dried at 105° — 110° to a constant weight. Aliquot quantities of the dried salts were ignited to thoria. The results showed that no reproducible results could be obtained by the direct weighing of the precipitates, although the same precipitates, when ignited to thoria gave reliable values. The formulas obtained in three cases are entirely different and they are given in Table VIII.

TABLE VIII

FORMULAS OF THE THORIUM SALTS OF ARYL FATTY ACIDS

Th-salt of phenylacetic acid	Th-salt of phenylpropionic acid	Th-salt of 1-naphthylacetic acid
$(C_8H_7O_2)_3$-Th(OH)	$(C_9H_9O_2)_2$-Th-$(OH)_2$	$(C_{12}H_9O_2)$-Th$(OH)_3$

All the thorium salts are soluble in dilute mineral acids. Though they are highly soluble in ammonium carbonate solution, they are not soluble in presence of ammonium ions of other ammonium salts.

Separation of thorium from Indian monazite *

Monazite sand was extracted with sulphuric acid by adopting the procedure of RAGHAVA RAO[5]. Thorium and rare earths present in this solution were converted into their nitrates after removal of phosphoric acid. This solution was rendered neutral to Congo red and thorium was precipitated from it by the three acids, as described before. The results were compared with those obtained by *m*-nitrobenzoic acid and are given in Table IX.

TABLE IX

EXTRACTION OF THORIUM FROM INDIAN MONAZITE

Acids employed	Expt. No.	Wt. of the sample	Wt of ThO_2 obtd.	% recovery of ThO_2
m-Nitrobenzoic acid	1	1.320 g	0.0965 g	7.31
,,	2	1.255	0.0918	7.32
,,	3	1.232	0.0902	7.32
Phenylacetic acid	1	1.320	0.0966	7.32
,,	2	1.255	0.0918	7.32
,,	3	1.232	0.0899	7.30
Phenylpropionic acid	1	1.320	0.0965	7.31
,,	2	1.255	0.0918	7.32
,,	3	1.232	0.0901	7.31
1-Naphthyl acetic acid	1	1.320	0.0964	7.30
,,	2	1.255	0.0916	7.31
,,	3	1.232	0.0901	7.31

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* The sample was supplied by the Govt. of India, Ministry of Natural Resources and Scientific Research for analysis.

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DISCUSSIONS

1. Of the three acids, namely phenylacetic-, phenylpropionic- and 1-naphthylacetic acids, phenylacetic acid is the most suitable reagent for the gravimetric determination of thorium. The thorium-precipitate obtained by this acid is flocculent and settles quickly, even without the addition of ammonium acetate as electrolyte, whereas, in case of the other two acids, addition of ammonium acetate is essential to obtain the thorium precipitate in the form in which it can be filtered.

2. The voluminous nature of the precipitate obtained with phenylacetic acid is advantageous in the detection and determination of small quantities of the element, although direct weighing is not possible. As little as 0.0004 g of thorium can be determined with this acid, while phenylpropionic- and naphthylacetic acids can precipitate effectively up to 0.01 g and 0.02 g of thorium respectively from its solution.

3. From pH studies, it has been found that the thorium can be quantitatively precipitated from its solutions with phenylacetic acid in a wider pH ranges from 2.8 and higher whereas, the phenylpropionic- and naphthylacetic acids begin to precipitate thorium completely from pH 3.6 and 4.4 respectively.

4. The aryl fatty acids may be used for the separation of thorium from cerite earth mixtures and also from monazite sand. Phenylacetic acid can precipitate thorium from solutions having thoria-rare earth oxide concentration up to 1:40, by double precipitation method, without any contamination. This ratio for phenylpropionic and 1-naphthylacetic acids, are only 1:16 and 1:14 respectively.

5. These aryl fatty acids also act selectively in the presence of many of the foreign ions normally appearing with thorium, the presence of some of course, required double precipitation. Thorium can be separated by phenylacetic acid from solutions having a ThO_2:U_3O_8 ratio up to 1 : 50, by double precipitation and hence this acid can be utilised for the purposes of assay of uranium minerals for thorium. Iron, mercury and zirconium are co-precipitated along with thorium by all the three acids.

6. It is interesting to note that each thorium salt of the three acids is a basic type of compound, which differs entirely in composition from the others. The direct weighing method cannot be applied with these reagents.

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SUMMARY

Phenylacetic-, phenylpropionic- and 1-naphthylacetic acids show definite promise as precipitating agents for the gravimetric determination of thorium. They can separate thorium from cerite earth and monazite sand, from solutions having thoria: rare earth oxide ratio up to 1 : 40, 1 : 16 and 1 : 14 respectively, by a double precipitation method. Foreign ions such as calcium, barium, strontium, titanium, zinc etc. do not interfere in the determination of thorium by these reagents. As the thorium salts of these three acids are basic in nature, each possessing an entirely different composition, the determination of thorium by direct weighing of the precipitates is not possible and in each case the ignition of the precipitate to thoria is essential.

RÉSUMÉ

Les acides phénylacétique, phénylpropionique et 1-naphtylacétique peuvent être utilisés pour le dosage gravimétrique du thorium. Ils permettent la séparation par double précipitation du thorium d'avec les terres cériques et de la monazite (rapports thorium — oxydes de terres rares 1 : 40, 1 : 16 et 1 : 14). Des ions étrangers tels que calcium, strontium, titane, zinc, etc. ne gênent pas. Le dosage par pesée directe des précipités obtenus n'est pas possible; les sels de thorium formés étant basiques et n'ayant pas de composition bien déterminée. Dans chaque cas il est nécessaire de griller le précipité pour obtenir l'oxyde de thorium.

ZUSAMMENFASSUNG

Die Phenylessigsäure, die Phenylpropionsäure und die Naphthylessigsäure können für die gravimetrische Bestimmung des Thoriums verwendet werden. Durch doppelte Ausfällung kann die Abtrennung des Thoriums von Ceriumelementen und von Monazit vorgenommen werden (Verhältnis Thorium — Oxyde der seltenen Erden 1 : 40, 1 : 16 und 1 : 14). Andere anwesende Ionen wie Calcium, Strontium, Titan, Zink usw. stören die Bestimmung nicht. Die Dosierung durch direktes Wägen der erhaltenen Niederschläge ist nicht möglich; die gebildeten Thoriumsalze sind basisch und haben keine konstante Zusammensetzung. In jedem Falle ist es notwendig, den Niederschlag zu kalzinieren, um Thoriumoxyd zu erhalten.

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ANALYSE ORGANIQUE FONCTIONNELLE

II. COMBINAISONS DU DIMÉDON (DIMÉTHYL-5,5 CYCLOHEXANEDIONE-1,3) AVEC LES ALDÉHYDES

par

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Dans ce deuxième Mémoire, nous avons préparé à l'état de pureté 26 aldéhydes appartenant à diverses séries et contrôlé leur pureté à l'aide du spectromètre infrarouge Perkin-Elmer C-12 équipé au sel gemme, dans la région spectrale comprise entre 6 et 15 μ. Ceci fait, nous avons précipité ces aldéhydes à l'aide du *dimédon*, réactif provenant soit de la firme Eastman-Kodak et repurifié par cristallisations, soit préparé par nous-mêmes.

Le mode de préparation des dimédonates est tout à fait classique: l'aldéhyde en solution alcoolique (sauf le formaldéhyde qui est pris en solution aqueuse) est traité par une solution hydro-alcoolique à 50% de dimédon (environ 3 mol. de réactif pour une d'aldéhyde); on porte pendant quelques minutes à 50° et laisse déposer, filtre ou centrifuge, lave avec une solution alcoolique diluée du réactif. On sait qu'un certain nombre de ces dimédonates ont été proposés pour l'analyse quantitative des aldéhydes après séchage à poids constant et pesée.

Nous avons alors tracé à l'aide de la thermobalance à inscription visuelle, les courbes de thermolyse de ces précipités en opérant depuis 20° jusqu'au voisinage du point de fusion, avec une vitesse de chauffe linéaire de 100 et de 150° par heure et avec un poids de substance allant de 60 mg à 150 mg. Les 26 composés aldéhydiques utilisés sont rangés dans le tableau ci-dessous avec le point de fusion que nous avons mesuré au bloc Maquenne pour les dimédonates correspondants. Dans l'autre colonne, nous indiquons la température de décomposition apparente telle qu'elle figure sur le graphique.

Quand on chauffe le dimédon lui-même (F: 148-149°), on observe qu'il est loin d'être stable jusqu'au point de fusion. Il commence à perdre du poids vers 107° avec la vitesse de chauffe indiquée et à 153°, la perte mesurée vaut 16.0 mg pour 126.2 mg de réactif.

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* Pour le 1er Mémoire de cette série, voir *Anal. Chim. Acta*, 10 (1954) 520.

DISCUSSION

Nous n'avons pas reproduit les enregistrements de thermolyse qui sont des droites parfaitement horizontales s'incurvant ensuite très rapidement quand la décomposition a commencé. Aucun dimédonate, parmi ceux que nous avons choisis, ne retient de réactif en excès. Les décompositions ne se montrent pas explosives. Les dimédonates sont beaucoup moins stables que les dinitro-2,4 phénylhydrazones, mais ils sont moins solubles et, à condition d'effectuer le séchage en deça des températures indiquées, les dosages sont corrects.

Aldéhyde étudié	fusion	Points de décomposition du dimédonate
Formaldéhyde	189°	157°
Acétaldéhyde	144°	161°
n-Propionaldéhyde	156°	158°
n-Butyraldéhyde	134°	142°
Crotonaldéhyde	210°	165°
n-Heptanal	101°	183°
n-Octanal	88°	104°
n-Nonanal	84°	94°
n-Décanal	77°	85°
Glyoxal (bidimédonate)	223°	169°
Benzaldéhyde	197°	185°
o-Chlorobenzaldéhyde	206°	172°
p-Chlorobenzaldéhyde	155°	180°
Dichloro-3,4 benzaldéhyde	180°	184°
m-Nitrobenzaldéhyde	196°	196°
Cuminaldéhyde	171°	187°
Vératraldéhyde	161°	161°
Cinnamaldéhyde	212°	150°
Salicylaldéhyde	219°	216°
Aldéhyde méthoxy-2 naphtoïque-1	247°	233°
„ „ -4 „ -1	202°	202°
Vanillal	195°	195°
n-Dodécyl-vanillal	75°	133°
Furfural	162°	162°
α-Thiénylaldéhyde	171°	161°
Pyrénylaldéhyde-3	121°	152°

Il est difficile de tirer des règles de la stabilité des dimédonates; nous pouvons simplement remarquer qu'en série acyclique, les températures mesurées s'abaissent quand s'accroît la longueur de la chaîne.

Certains des points de fusion diffèrent parfois considérablement de ceux d'auteurs antérieurs surtout dans le cas de l'heptanal, de l'octanal, du nonanal et du décanal normaux. La spectrographie infrarouge ne décèle pas d'isomères ramifiés et pas de trace d'alcool primaire résiduel dans nos dérivés. Nous voyons aussi l'influence considérable de la fixation d'une chaîne en C_{12} sur la fonction phénol libre du vanillal.

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RÉSUMÉ

Les auteurs ont tracé et étudié les courbes de thermolyse du dimédon et des composés qu'il fournit avec 26 aldéhydes très divers dont la pureté avait été rigoureusement contrôlée par spectrographie infrarouge.

SUMMARY

The authors have traced and studied the thermolysis curves of dimedone and of the compounds it forms with 26 very different aldehydes. The purity of the aldehydes have been rigorously checked by infrared spectrography.

ZUSAMMENFASSUNG

Die Autoren haben die thermolytischen Kurven aufgezeichnet und studiert, welche von der Thermolyse des Dimedons und 26 seiner Verbindungen mit ganz verschiedenen Aldehyden stammen. Die Reinheit dieser Stoffe wurde mit Hilfe der Infrarotspektrographie genau kontrolliert.

Reçu le 21 juin 1954

DOSAGE COLORIMÉTRIQUE DU FER

par

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INTRODUCTION

L'addition d'un colorant bleu modifie les teintes développées par le fer avec le thiocyanate ou l'*a-a'* dipyridyle, créant ainsi une gamme allant du rouge au bleu en passant par la teinte sensible violette.

La détermination de cette teinte sensible permet le dosage de très petites quantités de fer.

Nous utilisons comme colorant bleu: avec le thiocyanate une solution de bleu de méthylène à $0.10^0/_{00}$ ou $0.05^0/_{00}$, ou une solution de sulfate d'indigo à $0.25^0/_{00}$ ou $0.10^0/_{00}$ ou $0.05^0/_{00}$. Avec l'*a-a'*-dipyridyle (qui donne des teintes moins intenses que le thiocyanate): une solution de bleu de méthylène ou une solution de sulfate d'indigo à $0.05^0/_{00}$.

RÉSULTATS DES EXPÉRIENCES

Détermination de la limite de perceptibilité

Des échelles de teintes sont effectuées avec des tubes identiques contenant chacun le même volume (10 ml) de solution de fer, et le même nombre de gouttes (10) de solution colorante. Nous constatons que la limite de perceptibilité correspond:

avec le thiocyanate, à une variation de 0.05 γ par ml,

avec l'*a-a'* dipyridyle, à une variation de 0.01 γ par ml.

De plus, la détermination du seuil de sensibilité nous a montré que pour une quantité croissante de colorant, la teinte obtenue est fonction de la quantité de fer, et inversement pour une quantité croissante de fer, la teinte obtenue est fonction de la quantité de colorant.

Dosage avec le thiocyanate

Nous opérons en milieu chlorhydrique, en présence d'eau oxygénée. Nous constituons une série d'échelles identiques avec des solutions de teneurs croissantes en fer, nous aboutissons aux conclusions suivantes:

a) Pour une quantité de fer donnée, l'addition d'un même volume de solution colorante développe toujours la même teinte.
b) Le volume de solution de colorant nécessaire pour développer la même teinte est fonction de la quantité de fer.
c) Dans le cas de teintes trop intenses, pour lesquelles l'oeil est insensible, il convient de ramener par dilution la concentration en fer entre 0.5 et 1 γ par ml pour que la méthode retrouve sa sensibilité.

Donc, à condition d'avoir préalablement établi une échelle (par addition à des quantités connues de fer, de volumes de colorants nécessaires pour créer une teinte identique), la quantité de colorant qu'il faudra ajouter à la solution de titre inconnu pour avoir une teinte sinon la même, tout au moins voisine de celle de l'échelle, déterminera la quantité de fer contenue dans la prise d'essai.

L'échelle établie pour la teinte obtenue par le thiocyanate d'ammonium fait apparaître que le nombre de gouttes de colorant indique (à un maximum plus ou moins 1 γ près), la quantité de fer dans la prise d'essai.

C'est suffisant pour fixer sur l'importance qu'il convient de lui donner pour effectuer une détermination quantitative dans les limites du maximum de sensibilité.

TABLEAU I

Volume de solution de fer		10 ml
additionnés de	ClH d = 1.18;	6 gouttes
	Solution de thiocyanate d'ammonium à 20%	2 ml
	Eau oxygénée à 20 volumes	6 gouttes.

γ de fer dans 10 ml	Nombre de gouttes normales de colorant pour obtenir la teinte sensible avec une solution de:		
	Bleu de méthylène à 0.05 ‰	Sulfate d'indigo à 0.25 ‰	Sulfate d'indigo à 0.05 ‰
20	32	24	
10	22	11	
9	20	10	
8	17	8	
7	15	7	
6	14	6	30
5	12	5	26
4	9	4	22
3	8		16
2	7		14
1	6		8
0.5	4		5

PRINCIPE DE LA DÉTERMINATION QUANTITATIVE

Les volumes du milieu réactionnel et des réactifs, ainsi que les concentrations de ces derniers étant constants, la même teinte sera obtenue indifféremment par addition d'un nombre *n* de gouttes de colorant à une quantité *q* de fer, ou par addition d'une quantité *q* de fer à un nombre *n* de gouttes de colorant.

Il s'ensuit que l'on pourra procéder à une détermination quantitative par application de la méthode des teintes sensibles telle qu'elle est pratiquée dans le dosage du plomb par la dithizone.

MODE OPÉRATOIRE

Réactifs. Acide chlorhydrique pur de densité d = 1.18
Eau oxygénée à 20 volumes
Solution de thiocyanate d'ammonium à 20%
Solution de sulfate d'indigo à 0.05‰.

Solution titrée. Solution-mère de chlorure ferrique à 1 g de fer ‰ dosée pondéralement, à partir de laquelle nous préparons par dilution les solutions de titre connu.

Sur un volume connu, qui doit renfermer tout le fer à l'état de $Fe^{(III)}$, on détermine préalablement le nombre de gouttes de la solution d'indigo nécessaires pour créer la teinte sensible prise dans la gamme des violets. Si la teinte est trop intense, et si l'on n'a pas établi d'échelle donnant les teneurs approximatives, on détermine expérimentalement la quantité d'eau qu'il conviendrait d'ajouter à la prise d'essai pour avoir une intensité de teinte compatible avec la précision que l'on recherche.

Dans un bécher de 50 ou de 100 ml de forme haute, on fait s'écouler la prise d'essai, que l'on dilue si nécessaire d'un volume d'eau connu: V ml. Le volume total ne doit pas être inférieur à la moitié de la capacité du bécher.

On ajoute alors successivement:
0.5 ml de ClH d = 1.18
4 ml de solution de thiocyanate à 20%
0.5 ml d'eau oxygénée à 20 volumes
puis,
le nombre de gouttes de solution d'indigo tel qu'il a été fixé par l'essai préalable.

Dans une second bécher identique au premier, on met un volume d'eau égal à celui de la prise d'essai et V ml d'eau de dilution. Après avoir ajouté les réactifs, on fait s'écouler à l'aide d'une microburette la solution — type de fer à 10 γ par ml, jusqu'à obtention d'une teinte identique à celle du contenu du premier bécher.

Il est évident que le volume de la solution-type de fer ne doit pas être tel qu'il entraîne un accroissement de volume susceptible de fausser l'intensité de la teinte. C'est pourquoi il est préférable de disposer d'une échelle qui permette d'après les indications de l'essai préalable, de fixer l'importance de la prise d'essai en fonction du titre de la solution-type.

Les teintes étant développées dans les mêmes volumes et avec les mêmes quantités de réactif, un essai à blanc n'est pas nécessaire.

Dosage avec l'a-a' dipyridyle

Le dosage du fer par l'*a-a'* dipyridyle a été exposé dans une précédente communication[1], dans la méthode décrite ici il faut tenir compte de la décomposition du colorant bleu par l'hydrosulfite. Il faut donc détruire le léger excès d'hydrosulfite par ébullition de la solution jusqu'à disparition du précipité de soufre qui se forme tout d'abord, tout en protégeant le fer de toute oxydation par une addition immédiate de 10 ml d'une solution à 10% de chlorhydrate d'hydroxylamine, à la liqueur devenue limpide.

Après refroidissement, nous ajoutons 1 ml de solution d'*a-a'* dipyridyle à 0.5% et 10 ml de solution de chlorhydrate d'hydroxylamine. Le mode opératoire est calqué sur celui du dosage avec le thiocyanate; les résultats sont très bons.

L'observation des teintes se fait directement, mais elle est facilitée par l'emploi d'un bloc comparateur.

TABLEAU II

Volume de solution de fer 10 ml			
γ de fer dans 10 ml	Bleu de méthylène à 0.05 ‰	Sulfate d'indigo à 0.25 ‰	à 0.05 ‰
20	50 gouttes	30 gouttes	
10	24	12	
9	20	10	
8	18	9	
7	16	8	40 gouttes
6	14	7	35
5	13	6	30
4	12—13	5	25
3	12	4	20
2	11—12	3—4	15
1	11	2—3	12
0.5	6	2	8

RÉSUMÉ

Par développement d'une teinte sensible, il est possible de doser colorimétriquement de petites quantités de fer, sans avoir recours à un colorimètre. Le mode opératoire proposé dérive de celui utilisé pour le dosage du plomb, par la méthode à la dithizone.

SUMMARY

By developing a sensitive tint, it is possible to determine colorimetrically small quantities of iron without having recourse to a colorimeter. The proposed method is derived from that used for the determination of lead, by the dithizone method.

ZUSAMMENFASSUNG

Durch Entwicklung einer sensiblen Färbung wird es möglich, auf kolorimetrischem Wege kleine Quantitäten von Eisen zu bestimmen ohne Verwendung eines Kolorimeters. Die vorgeschlagene Arbeitsweise leitet sich von derjenigen ab, welche für die Bestimmung von Blei mit Dithizon verwendet wird.

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[1] M. GRAT-CABANAC, *Anal. Chim. Acta*, 5 (1951) 116 et 118.

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DIE UNIVERSELLE ANWENDUNG DER PHOTOMETRISCHEN KUPFERBESTIMMUNG DURCH EXTRAKTION DES DIÄTHYLDITHIOKARBAMAT-KOMPLEXES IN DER METALLANALYSE

EINE VERGLEICHSMESSUNG ZWISCHEN DEM ELEKTRO-PHOTOMETER VON ZEISS-OBERKOCHEN UND DEM EPPENDORF-PHOTOMETER VON NETHELER UND HINZ, HAMBURG

von

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Es wird die Kupferbestimmung durch Extraktion des Kupfer-Diäthyldithiokarbamat-Komplexes hinsichtlich des Einflusses der Störelemente Wismut, Nickel, Kobalt und Eisen überprüft, eine Arbeitsmethode gebracht und ihre universelle Anwendbarkeit auf die Untersuchung von Nichteisenmetallen und anorganischen Verbindungen durch Beleg-Analysen bewiesen. Gleichzeitig wurden bei dieser Gelegenheit Vergleichsmessungen zwischen dem Elektro-Photometer von Zeiss und dem Eppendorf-Photometer von Netheler u. Hinz, Hamburg durchgeführt.

Die Anwendung des Natriumdiäthyldithiokarbamat zur Bestimmung von Kupfer durch Extraktion des gebildeten gelbbraunen Komplexes mit organischen Lösungsmitteln wurde zuerst von CALLAN UND HENDERSON[1] beschrieben. Andere Autoren[2,3] haben weitere Untersuchungen darüber angestellt. Leider waren über den Einfluss der Störelemente Wismut, Nickel, Kobalt und Eisen nur unvollständige und widersprechende Angaben in der Literatur zu finden und es soll hier im Rahmen einer Vergleichsmessung zwischen dem Elektro-Photometer (Elko II) von Zeiss und dem Eppendorf-Photometer von Netheler u. Hinz dieser Einfluss genau festgestellt werden, um das Verfahren universell auf die Kupferbestimmung in Nichteisenmetallen und anorganischen Verbindungen anwenden zu können.

Zu diesem Zwecke wurden zunächst nach der Arbeitsmethode von ZIMMERMANN[4] aus Testlösungen von Kupfer, Wismut, Nickel, Kobalt und Eisen die Karbamat-Extrakte hergestellt und im Unicam-Quarzspektrophotometer S.P. 500 in 10 mm Quarzküvetten gegen Chloroform als Blindwert die in Abbildung 1 und 2 wiedergegebenen Absorptionskurven aufgenommen. Der Kupfer-Komplex zeigt ein Maximum bei 436 und 270 nm, Wismut nur bei 250 nm, Nickel bei 325 und 350 nm, Kobalt ebenfalls bei 325 und 250 nm und Eisen bei 267 nm.

Die entsprechenden Testlösungen wurden mit 5 ml Tarngemisch (20 ml 20%ige Zitronensäurelösung + 60 ml 10%igen Ammoniak + 10 ml 20%ige Ammoniumchloridlösung auf 100 ml H_2O) und 5 ml 0.2%ige wässrige Natriumdiäthyldithiokarbamat-Lösung versetzt und zwei bis dreimal mit etwa 10—15 ml Chloroform extrahiert. Die Extrakte wurden im 50 ml-Messkolben mit Chloroform bis zur Marke aufgefüllt. Daneben lief ein Chemikalien-Blindansatz den gleichen Arbeitsgang. Anschliessend wurden beide Extrakte durch trockne Filter (zum Zurückhalten

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der geringen Wassermengen) in trockne verschliessbare Erlenmeyer-Kölbchen filtriert und die Absorptionsmessungen ausgeführt. Das Schütteln des etwa 100 ml fassenden, birnenförmigen Scheidetrichters mit 5 mm langem Hals wurde durch eine kleine, schnellschwingende, elektrische Schüttelmaschine eigener Konstruktion besorgt.

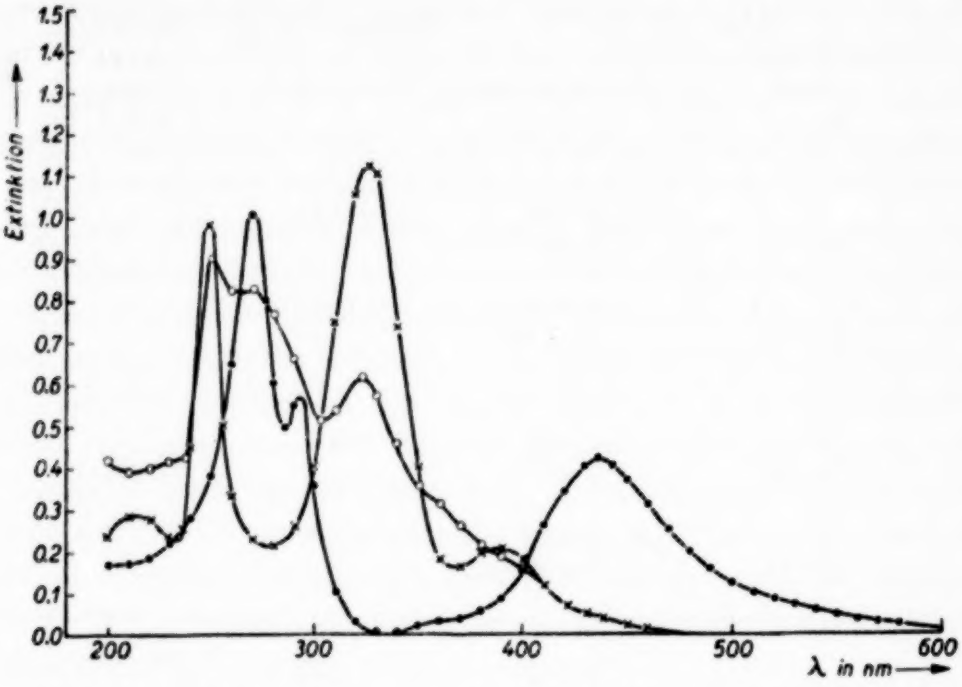

Abb. 1. Absorptionskurven von Kupfer-, Nickel- und Kobalt-„Carbamat"-Chloroform-Extrakten. Messung in 10 mm Schichtdicke.
100 µg Cu / 50 ml ●—●—●, Ni / 50 ml ×—×—×, Co / 50 ml O—O—O

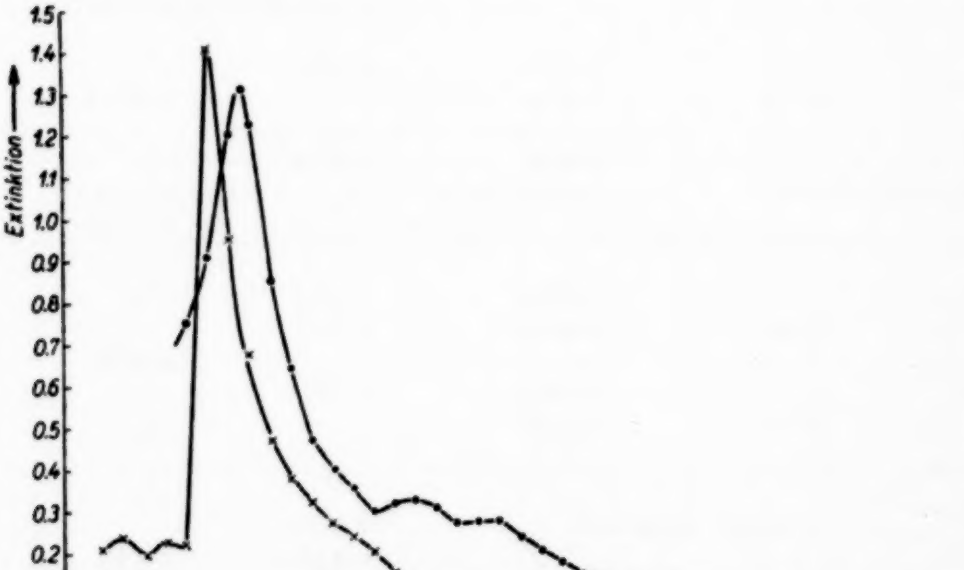

Abb. 2. Absorptionskurven von Wismut- und Eisen-„Carbamat"-Chloroform-Extrakten. Messung in 10 mm Schichtdicke.
100 µg Bi / 50 ml O—O—O, 1000 µg Fe / 50 ml ×—×—×

TABELLE I

MESSWERTE ZUR KUPFER-EINMESSKURVE

µg Cu in 50 ml	Elko II (1)		Eppendorf (2)	Mittelwert von 1+2	Bearbeiter
	Durchlässigkeit in %	Extinktion	Extinktion		
20	57.05	0.244 0.2437	0.245	0.2442	A
	57.04	0.244 0.2438	0.245		B
40	32.55	0.487 0.4874	0.487	0.4870	A
	32.61	0.487 0.4866	0.487		B
60	18.74	0.727 0.7272	0.727	0.7273	A
	18.73	0.727 0.7275	0.727		B
80	10.84	0.966 0.965	0.964	0.9651	A
	10.82	0.966 0.9656	0.964		B
100	6.24	1.205 1.205	1.205 1.205	1.205	A
	6.25	1.205 1.206	1.206		B
120	nicht messbar		1.459	1.459	A
	„ „		1.459		B
140	nicht messbar		1.678	1.678	A
	„ „		1.678		B

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Anschliessend wurden mit steigenden Mengen Kupfer-Testlösung (10 µg Cu/ml) die Einmesskurven am Elko II und Eppendorf-Photometer nach der gleichen Vorschrift unter Benutzung der Quecksilberlampen und des Sperrfilters 436 nm in 2 Küvetten von 30.000 mm Schichtdicke aufgestellt. Auf die Beschreibung des Messvorganges wurde verzichtet, da dieser hinreichend bekannt sein dürfte. Die Messungen wurden aus *einem* Ansatz in den gleichen Küvetten von zwei verschiedenen Beobachtern jeweils an beiden Geräten hintereinander ausgeführt und sind Mittelwerte aus 3 Messreihen mit je 3 Ablesungen. Die Ergebnisse gibt Tabelle I wieder. Für die Lösungen wurden Chemikalien zur Analyse und bidestilliertes Wasser verwendet. 25%iges Ammoniak wurde durch Einleiten von Ammoniakgas in bidestilliertes Wasser hergestellt. Aus den am Elko abgelesenen Durchlässigkeiten wurden die nebenstehenden Extinktionswerte berechnet. Die Abweichungen der Durchlässigkeiten lagen jeweils unter ±0.1%, während bei der Extinktion bis 1.0 die Streuung bei beiden Geräten ± 0.0002 und über 1.0 ± 0.005 nicht überschritt.

Die Messwerte stimmten sehr gut überein, graphisch und rechnerisch ergab sich eine Gerade, somit ist das LAMBERT-BEER'sche Gesetz für den Bereich von 0—140 µg Cu/50 ml streng erfüllt. Die Konzentration c [µg/50 ml] kann man auch mit einem aus den obigen Messwerten errechneten mittleren Eichfaktor b (= 82.64), bei Verwendung von 30 mm Schichtdicke und λ = 436 nm, durch Multiplikation mit der Extinktion E ermitteln.

Danach wurde der Einfluss der Störelemente Wismut, Nickel, Kobalt und Eisen überprüft. Steigende Mengen Testlösung der einzelnen Elemente wurden nach der gegebenen Vorschrift extrahiert und die Messwerte ermittelt, die in Tabelle II zusammengestellt sind.

TABELLE II

EINFLUSS DER STÖRELEMENTE

Gegeben	Störelement µg/50 ml	Gefunden und als µg Cu berechnet	Extinktion
100	Bi	5.0	0.060
1000		51.5	0.619
100	Ni	10.0	0.122
1000		96.5	1.165
100	Co	15.0	0.185
1000		über 230	über 2.5
100	Fe	1.0	0.013
1000		31.5	0.382

Bei Anwesenheit von je 4 mg der drei ersten Elemente lagen die Messwerte weit oberhalb des Messbereiches, während von 4 mg Eisen etwa 100 µg Kupfer vorgetäuscht wurden. War zusätzlich noch 0.1 g Aluminium vorhanden, ergaben schon 100 µg Eisen 37 µg Kupfer. Dieser vorgetäuschte Kupferwert kann entweder durch Zugabe von mehr Zitratlösung und Ammoniak oder durch Herab-

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setzen der Reagenzmenge verringert, aber nicht ganz beseitigt werden. Hier kann erwähnt werden, dass auch die Farbkonstanz der einzelnen Metallkomplexe überprüft wurde. So zeigte sich, dass die Messwerte des Wismut- und Kobaltkomplexes, wenn sie längere Zeit dem Licht der Quecksilberlampe ausgesetzt waren, abnahmen und nach Stehenlassen im Tageslicht auch wieder anstiegen. Die Komplexe von Kupfer, Nickel und Eisen zeigten die Erscheinung nicht und waren über 24 Std. konstant. Für eine genaue Kupferbestimmung wäre nach den erhaltenen Werten der bekannte Gehalt der anwesenden Störelemente notwendig, um ihn rechnerisch in Abzug bringen zu können.

Es soll nun an einigen Versuchen festgestellt werden, inwieweit der Störeinfluss der genannten Elemente beseitigt werden kann. Dazu fanden sich Hinweise in der unter[3] zitierten Arbeit, wo bei Anwesenheit von Wismut empfohlen wird, zunächst die Summe von Kupfer und Wismut zu bestimmen und dann in einem zweiten Ansatz 0.5 ml 0.5%ige Kaliumcyanid-Lösung zuzugeben, wodurch der Kupfer-Karbamat-Komplex zerstört und bei der anschliessenden Extraktion nur der Wismut-Komplex extrahiert wird. Eigene Kupferbestimmungen nach dieser Methode von verschiedenen Bleiproben mit wechselnden Wismut-Gehalten zeigten, dass diese Vorkehrung unnötig ist, da Wismut in Gegenwart von Blei nicht mitextrahiert wird. Als zusätzlicher Beweis wurde je 100 mg Blei als Bleinitrat-Lösung mit 100, 500 und 1000 µg Wismut als Wismutnitratlösung versetzt und wie beschrieben extrahiert. Die Messwerte lagen unter 1 µg Cu. Die gleichen Versuche unter Zugabe von 50 µg Kupfer ergaben den theoretischen Wert.

Der Einfluss des Nickels soll sich nach WILLMOTT UND RAYMOND[3] durch Zugabe von 0.5 ml 1%iger Dimethylglyoxim-Lösung zu der ammoniakalischen zitrathaltigen Lösung und Extraktion des gebildeten roten Nickelkomplexes durch Chloroform ausschalten lassen. Hierzu wurden aus Lösungen mit 50 µg Kupfer und 0.1: 0.5; 1 und 5 mg Nickel als Nitrat, das Nickel in der angegebenen Weise entfernt und anschliessend das Kupfer wie beschrieben bestimmt. Die Extraktionen erfolgten 10 min lang zwei bis dreimal mit je 10—25 ml Chloroform, bis dieses farblos blieb. Für 0.1 mg Nickel wurden 1 ml, für 1 und 5 mg Nickel mindestens 20 ml 1%ige ammoniakalische Dimethylglyoxim-Lösung benötigt, (diese bewährte sich besser als die übliche alkoholische Lösung) um das zugegebene Kupfer quantitativ wiederzufinden.

Nach den gleichen Autoren soll bei Anwesenheit von Kobalt dieses durch Dimethylglyoxim-Zusatz in der wässrigen Phase verbleiben und bei der nachfolgenden Karbamat-Extraktion nicht mitreagieren. Zur Kontrolle wurden Lösungen mit 50 µg Kupfer und 0.1; 0.5; 1 und 5 mg Kobalt als Nitrat in der angegebenen Weise behandelt; in allen Fällen wurde das zugegebene Kupfer quantitativ mit einem Fehler von ± 1 µg wiedergefunden.

Der Einfluß des Eisens sollte durch den Zitratzusatz ausgeschaltet sein. Bei eigenen Versuchen zur Kupferbestimmung in Aluminiumproben mit Eisengehalten von 0.3 bis 1.5% wurden Unstimmigkeiten zwischen den Ergebnissen der Karbamat-Methode und anderen Verfahren festgestellt. Da andere Elemente ausser Eisen in nennenswerten Mengen nicht vorhanden waren, konnte nur dieses die Störung verursachen; was auch die Absorptionskurve des Eisenkarbamat-Komplexes (Abb. 2) und die Vorversuche in Tabelle II bestätigen. Versuche, diesen Einfluss durch mehrmaliges Schütteln des Kupferkarbamat-Extraktes mit Ammoniak in wechselnder Menge und Konzentration, sowie über verschiedene Zeiträume auszuschalten, führten zum Erfolg. Die besten Ergebnisse wurden durch viermalige Extraktion mit je 30 ml Ammoniak (1+4) je 10 Minuten lang erzielt. Da die Operation umständlich sowie zeitraubend ist und zu Minderbefunden Anlass geben kann, wurde versucht, das Eisen mit Sulfosalicylsäure komplex zu binden; diese Bemühungen waren erfolglos und es wurde anschliessend „Komplexon" (Dinatriumsalz der Äthylendiamintetraessigsäure) angewendet, wie von Forster[5] und anderen Autoren in der neueren Zeit empfohlen wurde. Hierzu wurden 10 ml einer Lösung, die 50 g Äthylendiamintetraessigsäure und 50 ml, 25 %igen Ammoniak in 250 ml enthielt, benutzt. Gleichzeitig wurde gefunden, dass die Reagenzkonzentration auf das 10 fache erhöht werden muss, um eine quantitative Bestimmung zu gewährleisten. Dies ist bei Blei-und Zinkproben besonders wichtig, weil hier ein Teil des Reagens von diesen Metallen gebunden wird. Bei Versuchen mit 50 μg Kupfer unter Zusatz von je 4 mg Ni, Co und Fe, einzeln und im Gemisch, auch bei Gegenwart von 0.1 g Al und Anwendung von 10 ml der Komplexonlösung wurden stets die theoretischen Werte gefunden. 4 mg Wismut konnten dagegen durch Komplexon nicht maskiert werden. Da mit grösseren Wismutgehalten fast nur in Bleilegierungen gerechnet werden kann und diese hier nicht mitextrahiert werden, wie vorher gezeigt wurde, ist dies ohne Belang. Es konnte bei Anwesenheit von 0.2 g Pb, Zn, Al und Mg durch Komplexon kein Einfluss auf die Messergebnisse festgestellt werden.

Da die Reaktionsverhältnisse der Störelemente durch die vorangegangenen Versuche und durch geeignete Wahl der Arbeitsbedingungen festgelegt sind, sollen nun an Kupferbestimmungen in verschiedenen Analysenkontrollproben und anderen Proben, deren Kupfergehalte durch Schiedsverfahren[6] bestimmt wurden, überprüft werden, wie weit sich die Karbamat-Extraktion universell anwenden lässt. Zu diesem Zwecke wurden von jeder Probe 3 direkte Einwaagen (0.1—0.2 g) und 3 grosse Einwaagen (1—2 g), um Seigerungen auszuschalten, gemacht; diese durch geeignete Säurebehandlung in Lösung gebracht und direkt oder nach dem Auffüllen und der Abnahme aliquoter Teile die Kupfergehalte bestimmt, die in Tabelle III zusammengestellt sind.

Arbeitsvorschrift

Reagenzien. Salpetersäure (1.4) z.A.: Salzsäure (1.19) z.A.; Wasserstoffperoxyd 30% z.A.; Ammoniumzitratlösung (400 g Zitronensäure z.A. in etwa 500 ml Wasser lösen, mit 25 %igem Ammoniak gegen Lackmus neutralisieren,

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TABELLE III

BELEGANALYSEN ZUR KUPFER-BESTIMMUNG NACH DER „CARBAMAT"-EXTRAKTION

Probe Nr.	Zusammensetzung	Cu-Gehalt in %		Maximale Abweichung vom Mittelwert	Gerät	Einwaage
		Soll	Ist			
1	2% Sb 0.7% Sn 0.04% Bi Rest Pb	0.026	0.025	± 0.001	1 *	1 u. 0.1 g
			0.025	± 0.001	2 *	
2	0.5% Sb 0.004% Bi Rest Pb	0.105	0.109	± 0.004	1	0.5 u. 0.05 g
			0.109	± 0.004	2	
3	0.2% Sb 0.1% Bi Rest Pb	0.041	0.040	± 0.002	1	1 u. 0.1 g
			0.040	± 0.002	2	
4	10% Sb 0.02% Bi Rest Pb	0.0066	0.0065	± 0.0002	1	0.5 g
			0.0065	± 0.0002	2	
5	4% Al Rest Zn	0.079	0.081	± 0.001	1	1 u. 0.1 g
			0.081	± 0.001	2	
6	Reinstes Cd	0.001	0.0011	± 0.0001	1	1 g
	99.98%		0.0011	± 0.0001	2	
7	1.5% Fe 0.2% Si Rest Al	0.0040	0.0037	± 0.0008	1	2 u. 0.2 g
			0.0037	± 0.0008	2	
8	Rein Al	0.0017	0.0016	± 0.0001	1	1 u. 0.2 g
	99.8%		0.0016	± 0.0001	2	
9	0.2% Si 0.2% Fe Rest Al	0.0036	0.0036	± 0.0001	1	1 u. 0.2 g
			0.0036	± 0.0001	2	
10	10% Si 0.5% Fe 0.4% Mn Rest Al	0.009	0.0083	± 0.0002	1	1 u. 0.2 g
			0.0083	± 0.0002	2	
11	7% Mg 0.4% Fe 0.2% Mn Rest Al	0.026	0.023	± 0.0005	1	1 u. 0.2 g
			0.023	± 0.0005	2	

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* 1 = Elko II   * 2 = Eppendorf-Photometer

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TABELLE III (Fortsetzung)

Probe Nr.	Zusammensetzung	Cu-Gehalt in %		Maximale Abweichung vom Mittelwert	Gerät	Einwaage
		Soll	Ist			
12	3% Mg 0.2% Fe 0.2% Cr Rest Al	0.044	0.044	± 0.002	1	1 u. 0.2 g
			0.044	± 0.002	2	
13	6% Al 0.8% Zn Rest Mg	0.131	0.131	± 0.001	1	0.5 u. 0.05 g
			0.131	± 0.001	2	
14	Rein Zinn	0.006	0.0058	± 0.0002	1	1 g
	99.98%		0.0058	± 0.0002	2	
15	0.6% Al 0.2% Mn Rest Zn	0.54	0.545	± 0.002	1	0.5/0.01 g
			0.546	± 0.002	2	
16	3.5% Al	0.765	0.776	± 0.002	1	0.5/0.01 g
	Rest Zn		0.777	± 0.003	2	
17	4.8% Zn 2.5% Mg 0.5% Si Rest Al	0.98	0.993	± 0.030	1	0.5/0.01 g
			0.990	± 0.030	2	
18	1% Mg 0.5% Fe Rest Al	3.96	3.97	± 0.030	1	0.5/0.002 g
			3.97	± 0.030	2	
19	Graphit	0.001	0.0011	± 0.0001	1	2 g
	99.9% C		0.0011	± 0.0001	2	
20	Gummiasche 0.5% Fe Rest TiO_2	0.008	0.0081	± 0.0002	1	1 g
			0.0082	± 0.0002	2	

kühlen und auf einen Liter auffüllen); Ammoniak 25 % z.A.; 1 %ige wässrige Natriumdiäthyldithiokarbamatlösung z.A.; Komplexonlösung (50 g Tetraminessigsäure z.A. +50 ml 25 %igem Ammoniak z.A. mit Wasser auf 250 ml auffüllen); Chloroform z.A.

Analysengang. 0.1—1 g Einwaage (je nach Kupfergehalt und Gleichmässigkeit des Probematerials) werden in 1—5 ml Salpetersäure 1.4 (für Zn, Pb und Mg-Leg.) bezw. 1—10 ml Salzsäure 1.19 unter Zusatz von etwas Wasserstoffperoxyd oder

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Salpetersäure (für Al und Sn-Leg.) durch Erwärmen in Lösung gebracht und nach dem Verdünnen die Stickoxyde bezw. das überschüssige Wasserstoffperoxyd verkocht. Durchschnittseinwaagen werden entsprechend aufgefüllt und ein aliquoter Teil (in der Regel 0.1 g) in Arbeit genommen. Die direkte Einwaage oder Abnahme wird in einen 100 ml Scheidetrichter überführt, 2 ml Ammoniumzitratlösung, 10 ml Komplexonlösung zugegeben, mit 25 %igem Ammoniak gegen Lackmuspapier neutralisiert und dann 3 ml Ammoniak im Überschuss zugesetzt. Jetzt fügt man 10 ml 1 %ige Reagenzlösung, 25 ml Chloroform zu und schüttelt kräftig 10 Minuten lang. Nach dem Absitzen der Phasen wird der Chloroform-Extrakt in einen 50 ml-Messkolben abgelassen und die Extraktion noch mindestens zweimal mit je 10 ml Chloroform und 3-5 Minuten Schüttelzeit wiederholt, bis der letzte Extrakt farblos ist. Die vereinigten Extrakte werden im Messkolben mit Chloroform bei 20 °C bis zur Marke aufgefüllt. Ein Chemikalienblindansatz durchläuft daneben den gleichen Arbeitsgang. Beide Extrakte werden nach dem Durchmischen durch trockene Faltenfilter (12.5 cm Ø) in trockene verschliessbare Kölbchen filtriert. Anschliessend wird gegen den Blindwert der mehr oder minder gelbgefärbte Extrakt der Probe bei Quecksilberlampe und Sperrfilter 436 nm in 30—50 mm Schichtdicke gemessen. Den Prozentgehalt an Kupfer entnimmt man einer Einmesskurve, die man mit Kupfer-Testlösung ohne Zusatz von Fremdmetall unter den gleichen Bedingungen aufgestellt hat.

Beim Elektro-Kolorimeter reicht sie bei Benutzung einer Küvette von 30 mm Schichtdicke bis 100 μg Cu, beim Eppendorf-Photometer bis 140 μg Cu. Beide Kurven sind völlig gleich und erfüllen streng das LAMBERT-BEER'sche Gesetz. Will man vornehmlich kleine Gehalte bestimmen, arbeitet man zweckmässig mit 50 mm Schichtdicke, bei grösseren Gehalten mit 10 und 5 mm Schichtdicken.

Die Übereinstimmung der Analysenwerte nach der Extraktionsmethode mit den klassischen Schiedsverfahren ist als sehr gut zu bezeichnen, es wäre deshalb wünschenswert, wenn diese neue Methode als Schiedsverfahren eingeführt würde. Die Messwerte und ihre Reproduzierbarkeit an den beiden benutzten Geräten sind ebenfalls als ausgezeichnet anzusprechen. Das Elektro-Photometer von Zeiss und das Eppendorf-Photometer von Netheler u. Hinz können als Geräte zur genauen und absoluten Extinktionsmessung für den analytischen Chemiker sehr empfohlen werden.

An dieser Stelle möchte ich den Firmen Zeiss (Oberkochen) und Netheler u. Hinz (Hamburg) für die Überlassung der Geräte danken. Ferner sage ich Herrn Oberregierungsrat Dr. Ing. H. U. VON VOGEL für die Unterstützung der Arbeit meinen Dank und danke gleichzeitig Herrn SALEWSKI für die Hilfe bei der praktischen Ausführung.

ZUSAMMENFASSUNG

Die photometrische Kupferbestimmung als Kupfer-Diäthyldithiokarbamat-Komplex durch Chloroform-Extraktion wird einer Überprüfung auf den Einfluss der Störelemente Wismut, Nickel, Kobalt und Eisen unterzogen. Es wird eine Arbeitsanweisung gegeben und an 20 Beleganalysen von verschiedenen Materialien die

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universelle Anwendbarkeit bewiesen. Es lassen sich Kupfergehalte von 0.001—4.0% mit einem Analysenfehler von ± 10—0.5% bestimmen. Eine Einzelbestimmung mit Blindwert dauert etwa 40 Minuten. Ferner wurden Vergleichsmessungen zwischen dem Elektro-Photometer von Zeiss und dem Eppendorf-Photometer von Netheler u. Hinz mit diesem Analysenverfahren angestellt, wobei mit beiden Geräten völlige Übereinstimmung der Messwerte erzielt wurde.

RÉSUMÉ

Lors du dosage photométrique du cuivre par extraction au chloroforme du diéthyldithiocarbamate de cuivre, l'influence du bismuth, du nickel, du cobalt et du fer a été examinée. Vingt exemples d'analyses sont donnés. On peut doser ainsi 0.001—4.0% de cuivre avec une erreur de ± 10—0.5%. Un seul dosage avec une substance inconnue demande 40 minutes. De plus des mesures de comparaison ont été effectuées avec l'électrophotomètre de Zeiss et le photomètre Eppendorf de Netheler et Hinz, ces deux appareils donnent des résultats identiques.

SUMMARY

The influence of bismuth, nickel, cobalt and iron on the photometric determination of copper by chloroform extraction of copper diethyldithiocarbamate has been studied. Twenty examples of analyses are given. 0.001—4.0% of copper can be determinad to within 10—0.5%. A single determination of an unknown substance takes 40 min. Most of the measurements by comparison have been carried out with the Zeiss electrophotometer and the Eppendorf photometer of Netheler and Hinz; these two apparatus give identical results.

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SPECTROPHOTOMETRIC TITRATION OF CALCIUM AND MAGNESIUM WITH COMPLEXON-III AND METAL-SPECIFIC INDICATORS

by

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INTRODUCTION

According to our previous publication[1] the course of the extinction during the titration is represented by:

$E_t = \varepsilon'.l.i_t + (\varepsilon\text{-}\varepsilon').l.a.i_t$, in which

E_t = total extinction of the solution to be titrated
ε = molar extinction coefficient of the metal-free indicator
ε' = molar extinction coefficient of the metal-containing indicator
l = length of the light path through the solution to be titrated
i_t = total concentration of the indicator
i = concentration of the metal-free indicator
$a = \frac{i}{i_t}$ (a is a complex function of the volume of reagent added)

If however, we refer the extinction to the light intensity originally transmitted at the beginning of the titration (instead of to the intensity of the incident radiant energy, as is normally done), we may write: $E = (\varepsilon\text{-}\varepsilon').l.a.i_t$, and call E the relative extinction.

It is advisable so to choose the wavelength of the transmitted light that the absolute value of $(\varepsilon\text{-}\varepsilon')$ is at its maximum, because the accuracy is enhanced by this.

The end-point of the titration to be derived from the curve will be the sharper according as, during the titration, the four conditions resulting from our theoretical observations are better satisfied. Owing to dilution of the solution, resulting from the titration, both before and after the break in the extinction the curve will not be horizontal, but will exhibit a slight slope, which might be remedied by an altered arrangement[2].

EXPERIMENTAL TECHNIQUE

Performance of the measurement

The solution to be titrated is introduced into the cell and diluted with water; the indicator and reagents for the adjustment of the pH are added, the galvanometer is set at its initial value by means of the diaphragm, and the titration solution is added with constant mechanical stirring (apparatus: see Fig. 1). One minute after each addition the galvanometer is read. As soon as changes of colour begin to appear, perceptible from the behaviour of the galvanometer, the quantities of titration solution to be added are decreased. After completion of the measurement the galvanometer readings are converted into relative extinctions, and the latter are then plotted against the volume of the complexon-III solution added. It is also possible at once to plot the logarithm of the galvanometer deflections against the volume.

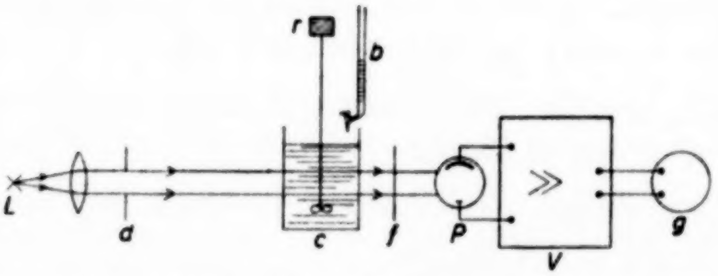

Fig. 1. L = mercury vapour lamp, d = diaphragm, c = absorption cell (capacity 300 ml, cell thickness 37 mm), r = stirrer, b = semimicroburet, f = interference filter, P = phototube, V = amplifier, g = galvanometer.

Reagents

Murexide solution. We have found that murexide in dissolved condition is not very stable (see also[3]), but is still unstable even in solid condition. Sometimes solid murexide contains only a small percentage (20%) of acid ammonium purpurate and a large amount of uramil, alloxantin, etc. (see *e.g.*[4]). The murexide content of commercial preparations was roughly determined by us by titration with $TiCl_3$ and by the photometric method. The instability of murexide makes it somewhat difficult and uncertain to satisfy condition 3, where a concentration of approximately 10^{-4}-10^{-5} molar in the solution to be titrated is theoretically considered. Ultimately 40 mg of murexide are shaken with 10 ml of water, and the saturated solution is filtered; this aqueous solution can be kept for at most one week.

Eriochrome black T solution. Eriochrome black T is much more stable than murexide, and the solution of 40 mg of the dye in 10 ml of 96% alcohol is also more stable; for greater security a certain amount of hydroxylamine hydrochloride is sometimes added.

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Phthalein complexon solution. 25 mg of dye + 0.2 ml of 4*N* ammonia are dissolved with water to a volume of 25 ml. This 0.1% indicator solution is considerably more stable than a murexide solution, but, like the Ca and the Mg compound, still exhibits at pH 10 a decrease in the extinction with time.

Titration solution. 0.1 molar complexon-III solution.

In order to obtain a 0.1 molar solution, 9.3025 g of complexon-III is dissolved in 250 ml of water, and according to the literature this solution need not be standardized (see on the other hand[5]). Upon standardization by different methods (visual with murexide to a standard Ni solution, potentiometric to a standard Fe(III) solution, alkalimetric to phenolphthalein or potentiometric, either after addition of an excess of Ca or not, determination of Na as Na_2SO_4 by gravimetric means) the complexon-III at our disposal was found to be slightly contaminated with the tri-sodium salt.

Sodium hydroxide solution. Approximately *N* NaOH solution.

Ammonia buffer solution. 35 ml of concentrated ammonia (s.g. 0.91) + 5.4 g of ammonium chloride + water up to 100 ml (pH 10).

Ca solution. A $CaCl_2$ solution, the content of which had been gravimetrically determined to be 0.802 mg of Ca/ml.

Mg solution. A $MgCl_2$ solution, the content of which had been gravimetrically determined to be 1.165 mg of Mg/ml.

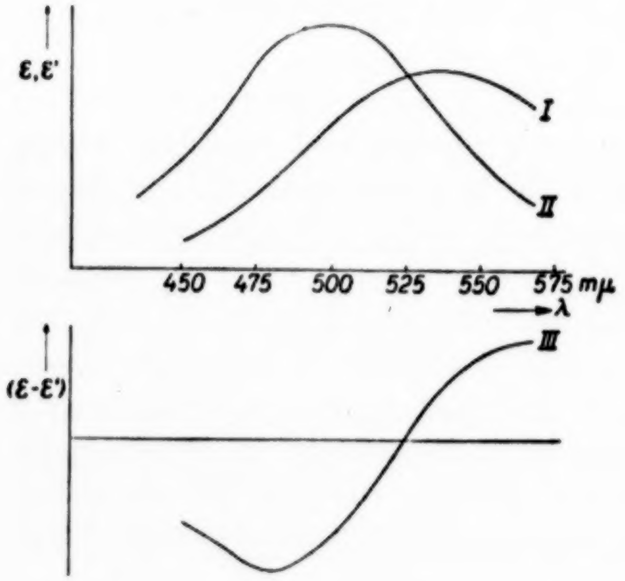

Fig. 2. I: ε (murexide) as function of λ
II: ε' (Ca-murexide) as a function of λ
III: $(\varepsilon$-$\varepsilon')$ as a function of λ

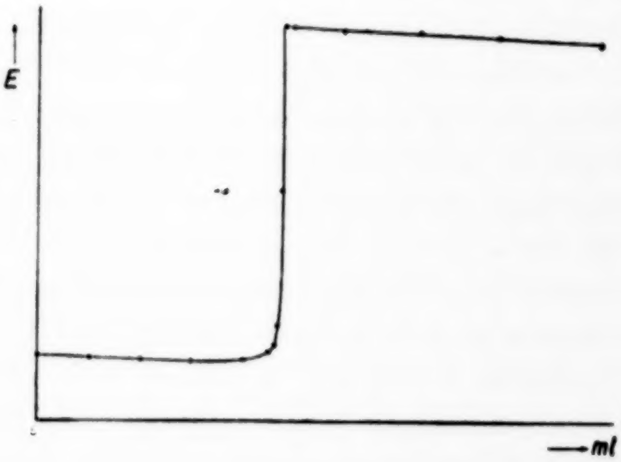

Fig. 3. Ca titration, using murexide as indicator.

CALCIUM DETERMINATION WITH COMPLEXON-III, USING MUREXIDE AS INDICATOR

According to our derivation, in order to obtain a sharp end point the two first conditions ($^*K_c \gg {}^*K_I$ and $^*K_I$ large) are undoubtedly fulfilled, while the two last requirements (i_t low and m_t high) can easily be satisfied in carrying out the determination.

Considering the value of (ε-ε') as a function of the wavelength, derived from the extinction curves for murexide and Ca-murexide (see Fig. 2), recorded with the spectrophotometer of JEAN AND CONSTANT, the wavelength ranges most suitable for our purposes are those at about 480 and about 580 mμ. For our titrations we chose 580 mμ.

Directions

After addition of about 120 ml of water, 7.5 ml of N NaOH solution (for adjustment to pH 12), and 1 ml of murexide solution, 25 ml of Ca solution are titrated with 0.1 molar complexon-III solution until the indication of the galvanometer shows practically no further change.

Result

The accompanying curve (Fig. 3) is a specimen of the titration graphs obtained by us. The decomposition of murexide in the strongly alkaline medium causes a certain additional decline in the "horizontal" parts of the curve; it is therefore advisable to carry out the titration in a short space of time.

MAGNESIUM DETERMINATION WITH COMPLEXON-III, USING ERIOCHROME BLACK T AS INDICATOR

Here we have to consider for a moment how far the first and the second condition for obtaining a sharp end-point are satisfied. From the numerical data at our disposal it can be derived in the same way as applied with murexide that $\log \frac{^*K_c}{^*K_I} \sim 3$, so that some rounding in the curve at the equivalence point is to be expected (see [1] Fig. 5).

At pH 9-10, $^*K_I$ has a value between $10^{4.5}$ and $10^{5.5}$, so that the second condition is fulfilled.

The third and the fourth condition can be met in carrying out the determination.

Considering the (ε-ε') values as a function of the wavelength, derived from the extinction curves for eriochrome black T and Mg-eriochrome black T (see Fig. 4), the wavelength ranges most suitable for our purposes are those at about 530 and about 630 mμ. We preferred the first range in connection with the possibility to use a Hg line (546 mμ) in the vicinity. Since (ε-ε') has a negative value at 546 mμ, $E = E(v)$ will range from high to low values, *i.e.* just the reverse from those at 630 mμ.

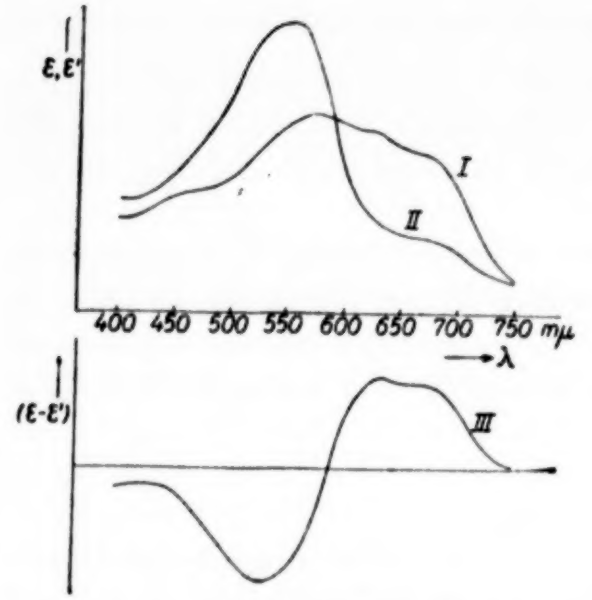

Fig. 4. I: ε (eriochrome black T) as a function of λ
II: ε' (Mg-eriochrome black T) as a function of λ
III: (ε-ε') as a function of λ.

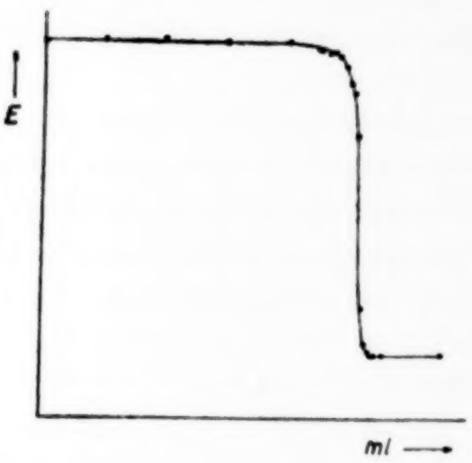

Fig. 5. Mg titration, using eriochrome black T as indicator.

Directions

After addition of about 120 ml of water, 7.5 ml of ammonia buffer (for adjustment to pH 10), and 1 ml of eriochrome black T solution, 20 ml of Mg solution are titrated with 0.1 molar complexon-III solution until the indication of the galvanometer shows practically no further change.

Result

The curve of Fig. 5 indeed exhibits the expected rounding.

SUCCESSIVE CALCIUM AND MAGNESIUM DETERMINATIONS IN THE SAME SOLUTION

Directions

After addition of murexide and adjustment to pH 12, Ca is titrated at 580 mμ. Dependent on the amount of Mg, a turbidity or a precipitate of $Mg(OH)_2$ is formed. This precipitate has little or no effect on the determination of the end-point of the Ca titration, and it is dissolved in hydrochloric acid before the Mg determination is started. Then the solution is neutralized, and adjusted to pH 10 by means of the ammonia buffer; eriochrome black T solution is added, and Mg is titrated at 546 mμ.

Result

The picture of the Mg titration is affected to some extent by the preceding Ca determination, for the murexide liberated after completion of the Ca titration reacts with Mg together with the eriochrome black T that is added. During the Mg titration the weak Mg-murexide complex will first lose its dye, and it is only in the vicinity of the equivalence point that the much more stable Mg-eriochrome black T complex will decompose. These two effects in combination give the following picture: first a rise of the extinction in consequence of the decomposition of the Mg-murexide complex. Then the more stable Mg-eriochrome black T complex also starts decomposing. There will then be a moment when the two effects neutralize each other. After this the second effect (the one which causes a drop) predominates, upon which the equivalence point is reached.

CALCIUM AND MAGNESIUM DETERMINATION RESP. WITH COMPLEXON-III, USING PHTHALEIN COMPLEXON AS INDICATOR

At the very moment our above investigation had been completed, the literature[6] mentioned a new and more stable metal indicator for the alkaline earths, *viz.* phthalein complexon. Thanks to the kindness of Prof. SCHWARZENBACH we obtained this dye, which we tested for its suitability for our spectrophotometric titration.

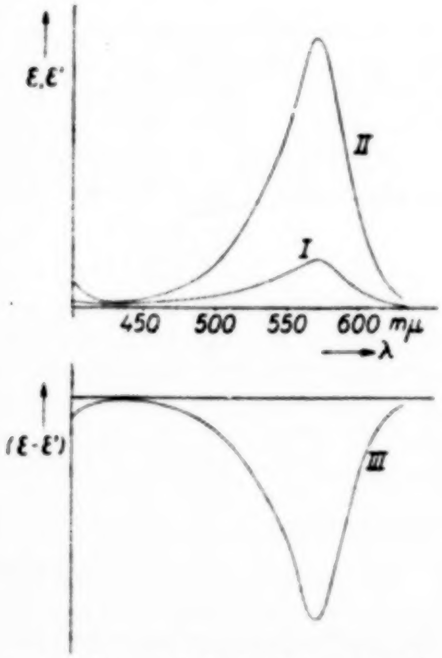

Fig. 6. I: ε (phthalein complexon) as a function of λ
II: ε' (Ca-phthalein complexon) as a function of λ
III: (ε-ε') as a function of λ.

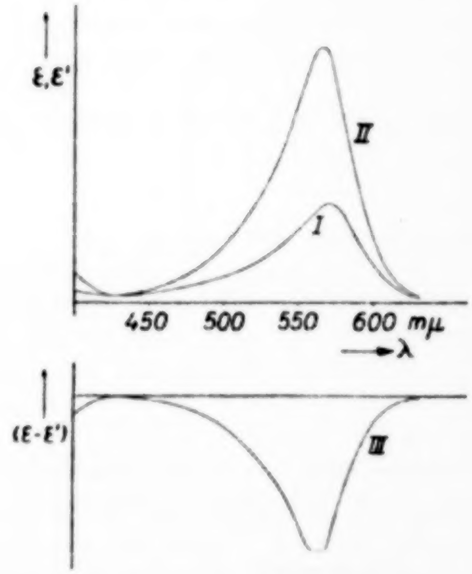

Fig. 7. I: ε (phthalein complexon) as a function of λ
II: ε' (Mg-phthalein complexon) as a function of λ
III: (ε-ε') as a function of λ.
(Fig. 7 has been drawn to a different scale from Fig. 6).

Considering the experiments of ANDEREGG *et al.*[6] it was only natural to carry out the Ca as well as the Mg titration at pH 10.

With Ca and Mg the dye gives compounds the absorption maxima of which, just like that of the dye itself, lie practically all in the same range, *viz.* 570-575 mμ (see Figs. 6 and 7); this involves difficulties for a visual titration, and an attempt has been made to circumvent this by adding alcohol to the titration medium. The extent of the extinctions indeed differs, in view of which our method can be applied without more ado. Both for Ca and for Mg we constructed the $(\varepsilon\text{-}\varepsilon')$ curves at the said pH. Here again the light source used was the mercury vapour lamp in combination with the filter of 546 mμ, and here, too, $E = E(o)$ will range from high to low values in relation to the negative value of $(\varepsilon\text{-}\varepsilon')$ at the wavelength in question.

Directions

After addition of about 120 ml of water, 7.5 ml of ammonia buffer (for adjustment to pH 10), and 1 ml of phthalein complexon solution, 25 ml of Ca solution or 20 ml of Mg solution are titrated with 0.1 molar complexon-III solution until the indication of the galvanometer shows practically no further change.

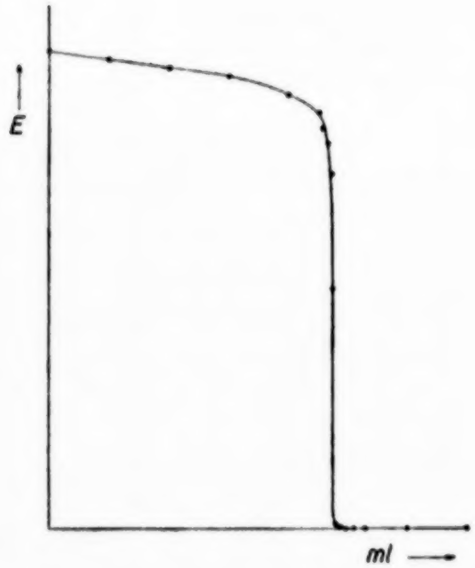

Fig. 8. Ca titration, using phthalein complexon as indicator.

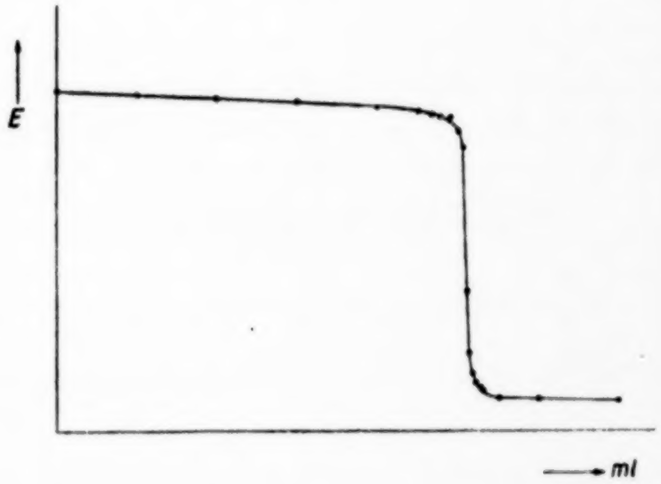

Fig. 9. Mg titration, using phthalein complexon as indicator.

The curves of Figs. 8 and 9 clearly show that the break at the equivalence point is considerably greater in the Ca titration than in the Mg titration, because the difference in extinction is greater for Ca than for Mg. The fact that the Mg titration curve exhibits only slight roundings indicates that the stability difference between the complexes of Mg with complexon-III and with the indicator is sufficient for a sharp determination of the end point; this contrasts with the statement of ANDEREGG *et al.*[6]

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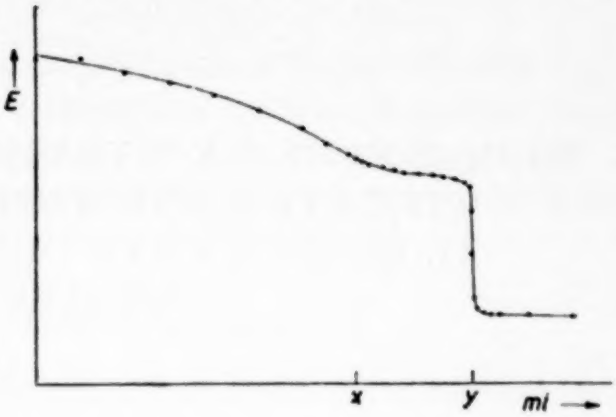

Fig. 10. (Ca + Mg) titration, using phthalein complexon as indicator; x = theoretical equivalence point for Ca, y = equivalence point for (Ca + Mg).

From the data about the stability constants[6] it appears that the titration of Ca in the presence of Mg is not very feasible, owing to the very slight difference in stability of the indicator complexes in question, so that at the very beginning of the titration the indicator is already bound to both the metal ions (see Fig. 10).

SUMMARY

The equivalence points of the Ca and Mg titrations with complexon-III, using metal-specific indicators, can be determined more accurately by the spectrophotometric than by the visual method. In comparison with the spectrophotometric method in the ultraviolet[7], where no indicator is required, the end point can be determined more sharply from our titration curve.

The accuracy is of the order of 0.5%; the repeatibility is even more favourable.

RÉSUMÉ

Les points d'équivalence des titrations de Ca et Mg, au moyen de complexon-III peuvent être déterminés par la méthode spectrophotométrique, celle-ci étant plus précise que la méthode visuelle. En comparant avec la méthode spectrophotométrique dans l'ultraviolet[7], sans indicateur, le point final peut être déterminé plus nettement dans notre courbe de titration. La précision est de l'ordre de 0.5%; la reproductibilité est même plus favorable.

ZUSAMMENFASSUNG

Die Äquivalenzpunkte der Titrationen von Ca und Mg mit Hilfe von Komplexon III können durch eine spektrophotometrische Methode bestimmt werden. Diese ist genauer als die visuelle Methode. Durch Vergleich mit dem spektrophotometrischen Verfahren im UV[7] ohne Indikator, kann der Endpunkt genauer ermittelt werden aus unserer Titrationskurve. Die Präzision ist von der Grösserordnung von 0.5%; der Bereich der Reproduzierbarkeit ist sogar noch kleiner.

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HIGH FREQUENCY TITRATIONS INVOLVING CHELATION WITH ETHYLENEDIAMINETETRA-ACETIC ACID.
II. QUANTITATIVE DETERMINATION OF SOME DIVALENT METALS

by

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Ethylenediaminetetra-acetic acid has been widely used in quantitative analysis as a titrant. It forms very stable chelates with most metals, except the alkali metals, and its reactions are both stoichiometric and rapid. Various methods are used for detecting the titrimetric end-points, the choice of method being dictated in some instances by the nature of the system under study. In some cases it is possible to use direct titrations in which color indicators are used[1,2,3,4,5] and where the ion being titrated has a distinctive absorption band, spectrophotometric methods may be employed for the end point detection[6,7,8]. Direct titrations are readily followed by conductometric and high frequency methods and some work along these lines is now under way[9,10]. Potentiometric, colorimetric, alkalimetric, and amperometric methods are applicable to titrations with ethylenediaminetetra-acetic acid and its salts[2,3,11,12,13,14] and have been the most widely used techniques for general applications.

In addition to the direct (compleximetric) titrations usually involved in the methods discussed above, indirect methods may be used. These procedures are based on the stoichiometric release of hydrogen ions through chelation with subsequent titration of the acid with standard base. This becomes a simple acid-base titration and any standard means can be employed for establishing the end-point.

EXPERIMENTAL

Reagents and chemicals. All of the chemicals used were of reagent or CP grade. The metal salt solutions were standardized using well established gravimetric procedures. Standard solutions of ethylenediaminetetra-acetic acid and its salts were obtained by dissolving appropriate amounts of reagent grade chemicals and standardizing the resulting solutions against calcium chloride and against pure salts of the metals under study. A buffer for pH 5.3 was prepared by mixing equal amounts of 0.2 *M* acetic acid and sodium acetate. A buffer for pH 7.0 was obtained by taking 11.88 g of $Na_2HPO_4.2H_2O$ and 9.078 g of KH_2PO_4, dissolving, and making up to one liter.

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Apparatus. The high frequency oscillator employed was a Sargent Model V Oscillometer which was used without the cell compensator (variable inductance unit). All titrations were performed in a large-type cell using an electric stirrer with all glass impeller for mixing. Hydrogen ion concentrations were established by means of a Beckman Model G pH meter.

Determinations of metals by titration of liberated hydrogen ions

Chelation results in stoichiometric amounts of hydrogen ions being released when cobalt, nickel, copper (II), zinc, cadmium, lead, and manganese (II) are mixed with ethylenediaminetetra-acetic acid. The chelates formed are composed of one mole of the chelating agent combined with a like amount of the metal ion, with 4 mole equivalents of hydrogen ion being liberated in the reaction[15]. For the metals enumerated, the hydrogen ions liberated are stoichiometrically related to the amount of metal ion reacting, and subsequent titrations with standard base yield quantitative measurement of the metal(s) present. While this method is not recommended for weakly chelating metals, such as the alkaline earths, thallium and silver, it does give excellent results with those metals forming stable complexes in acidic solution. As a typical case, the titration of nickel chloride is described.

One hundred milliliters of 1/3480*M* ethylenediaminetetra-acetic acid were placed in the titration cell of the Oscillometer and various amounts of nickel chloride were added. The hydrogen ions released by the added nickel were then titrated with 1/87*M* sodium hydroxide. The initial pH of the solution to be titrated was adjusted to be within the range of 5.3 to 5.5 and the concentration of ethylenediaminetetra-acetic acid was required to be in the range of 1/1000 to 1/5000*M* so as to bring the instrument response within its optimum range. Titration of the reagent yielded curves having characteristic sharp reversal points (blank), and titration of mixtures of the reagent and metal ions gave similar curves but with the reversal points displaced as the result of hydrogen ion liberation. The amount of displacement serves as a

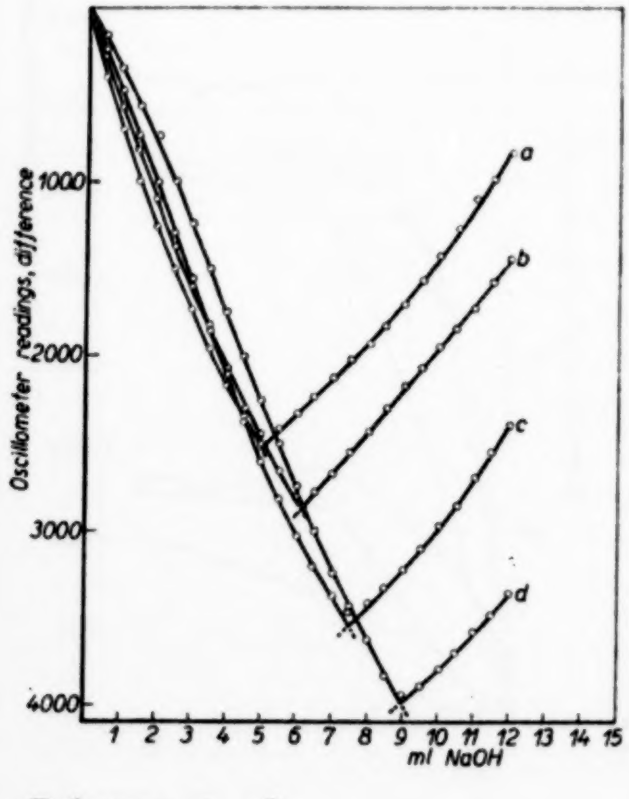

Fig. 1. Titrations of 1/3480*M* ethylenediaminetetra-acetic acid with 1/87*M* sodium hydroxide in the presence of nickel chloride.

a No addition of Ni
b 0.423 mg Ni added
c 0.846 mg Ni added
d 1.351 mg Ni added

direct measure of the amount of chelating metal present (Fig. 1). The presence of non-chelating or weakly chelating metals such as the alkali metals is without interference; and chloride, iodide, bromide, bromate, chlorate, iodate, nitrate, and thiocyanate do not interfere except in large amounts, whereupon they may cause a loading of the oscillator.

Determination of metals by direct titration with disodium ethylenediaminetetra-acetate

Under proper conditions ethylenediaminetetra-acetic acid forms 1 to 1 chelates with a large number of metals, the end-point being detectable by means of the high frequency oscillator. Because the free acid is relatively insoluble in water, the more soluble disodium salt is employed for direct titrations. Standardization can be made by titration against known amounts of pure metal or metal salts dissolved by appropriate means. Titrations are performed in either buffered or unbuffered media although the former generally gives the sharper end-points.

As a means of study, 100 ml portions of test solutions of metals to be investigated were titrated under various conditions. Because the sensitivity of instrument response is influenced by concentration, the initial study dealt with this problem. Solutions of cobalt, nickel, copper (II), zinc, cadmium, lead, and manganese (II) were prepared in concentration ranges of 1/200 to 1/12000*M* and titrated in unbuffered state. All of the curves obtained showed breaks at the equivalence points but the best results were obtained in the more dilute solutions (1/1000 to 1/6000*M*) as illustrated by the typical case of the titration of copper (II), shown in Fig. 2. Titrations performed to establish the optimum concentration ranges were made in unbuffered solutions except in the case of manganese (II) which gives distinct breaks only in buffered systems.

Because of the great stability of most of the complexes formed with ethylenediaminetetra-acetate, the use of buffers is not a necessity. Experience has shown, however, that more distinct reversals are obtained when buffers are present, and their use is therefore recommended. The acetate buffer of pH 5.3 is preferred in the titrations of cobalt, nickel, copper (II), zinc, cadmium, lead, and

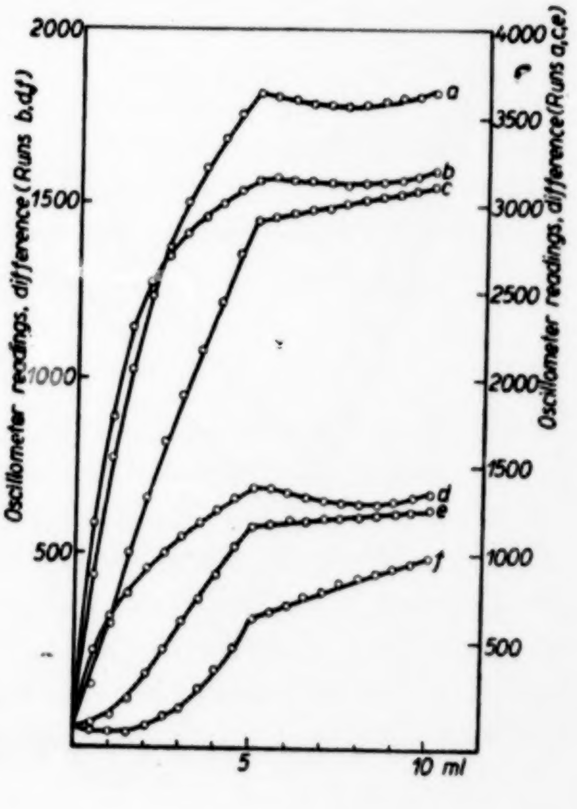

Fig. 2. Titrations of copper sulfate with disodium ethylenediaminetetra-acetic acid at various concentrations.

a 1/1000 *M* $CuSO_4$ with 1/50 *M* Na_2EDTA
b 1/400 *M* $CuSO_4$ with 1/20 *M* Na_2EDTA
c 1/3000 *M* $CuSO_4$ with 1/150*M* Na_2EDTA
d 1/200 *M* $CuSO_4$ with 1/10 *M* Na_2EDTA
e 1/6000 *M* $CuSO_4$ with 1/300*M* Na_2EDTA
f 1/12000*M* $CuSO_4$ with 1/600*M* Na_2EDTA

manganese (II). Calcium is best titrated in the presence of phosphate buffer (pH of 7). Because of loading effects, the amount of buffer used should be kept small so as to maintain instrument sensitivity. One ml of acetate buffer or two ml of phosphate buffer per 100 ml of sample is sufficient, provided the sample concentration is $1/3000M$ or less.

RESULTS

Titration curves for the various metals studied show great similarity as indicated by the typical curves illustrated in Fig. 3. Titrations in unbuffered solutions yield curves which ascend to an inflection indicating the end-point. The ascending portion of the curve results from the instrument response to hydrogen ions liberated during chelation. When titrations are conducted in buffered solutions, the curves show a negative slope due to the removal of metal ions through chelation. Because the hydrogen ions released from the reagent are immediately removed by buffer action, the instrument response must indicate a decrease in total ion concentration of the solution being titrated. A sharp reversal indicates the end-point in these titrations, the ascending portion of the curve resulting from the added reagent which quickly exerts a loading effect on the oscillator.

The reproducibility and accuracy of the titrations studied were found to be good. Typical results are shown in Table I. A somewhat restricted study was made of interference effects of diverse cations and anions. Because the reagent is essentially non-selective, it is to be expected that most metal ions will react similarly and will

TABLE I

REPRODUCIBILITY OF RESULTS

Cation	Molarity of titrant	Amount taken (mg)	Amount found (mg)	Per cent Error
Co	1/150	1.693	1.687	0.35
		1.693	1.690	0.18
		1.693	1.694	0.06
	1/302	0.547	0.543	0.73
		0.547	0.549	0.37
		0.547	0.545	0.37
Ca	1/150	1.336	1.332	0.30
		1.336	1.334	0.15
		1.336	1.330	0.45
	1/302	0.668	0.670	0.30
		0.668	0.663	0.75
		0.668	0.664	0.60

Determination of cobalt was carried out in acetate buffer.
Determination of calcium was carried out in phosphate buffer.

give mutual interferences. In certain cases, differences in stabilities of the chelates formed, however, do permit selective titrations. This can be illustrated by the titration of either cobalt, nickel, copper (II), zinc, cadmium, lead or manganese (II) in the presence of barium, strontium, silver, alkali metals and thallium (I). The latter metals do not interfere when the titrations are made in solutions buffered with the acetate buffer. Large amounts of any electrolyte will disturb the titrations, however, because of the loading of the oscillator which in turn reduces the sensitivity of the instrumental detection of end-points. The effect of adding various anions is generally negligible, provided they are compatible with the metal ions in solution. Loading effects are the most important source of error to be associated with the presence of anions.

Table II is presented to summarize the effects found in the case of titrations made with the co-existence of foreign electrolytes.

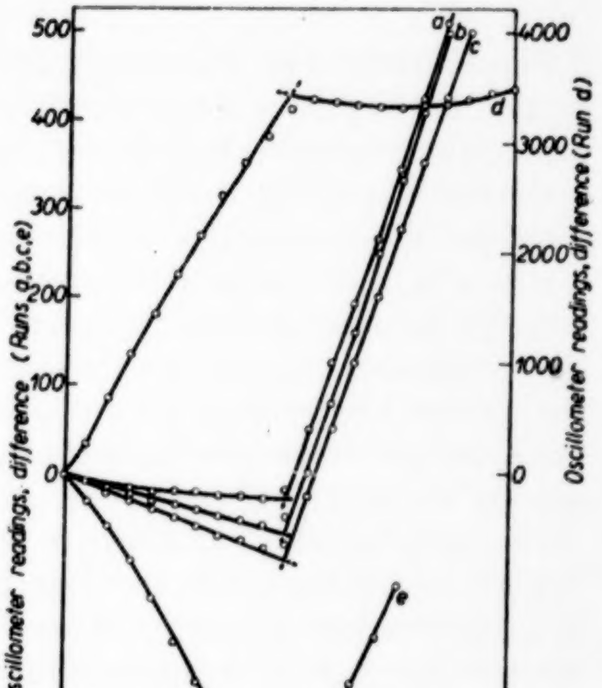

Fig. 3. Titrations of 1/3000M metal salts with 1/150M disodium ethylenediamine-tetra-acetic acid.

a Copper sulfate with acetate buffer
b Cadmium chloride with acetate buffer
c Cobalt chloride with acetate buffer
d Lead nitrate without buffer
e Calcium chloride with phosphate buffer

TABLE II

EFFECT OF ADDED ELECTROLYTES

Sample	Amount taken (mg)	Amount found (mg)	Foreign salt added (mg)	Per cent Error
Co	1.960	1.937	$AgNO_3$, 17.0	1.17
	1.960	1.941	KCl, 7.65	0.97
	1.960	1.948	KCNS, 9.70	0.61
Ni	1.952	1.940	K_2SO_4 5.8	0.67
	1.952	1.923	K_2SO_4, 17.4	1.49
	1.952	1.937	$BaCl_2$, 11.6	1.64
Pb	6.900	6.860	$TlNO_3$, 26.6	0.58
	6.900	6.836	$NaBrO_3$, 15.1	0.93

Note: Test solution, approximately 1/3000M; titrant, approximately 1/150M disodium ethylenediaminetetra-acetate; buffer, sodium acetate-acetic acid (pH 5.3).

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DISCUSSION

The high frequency oscillator provides an excellent means for detecting end-points in titrations employing ethylenediaminetetra-acetic acid or its salts. Such high frequency titrations are well suited to microchemical work, especially where it is desired to titrate minute amounts of metal ions in very dilute solution. By these methods, microchemical titrations are possible without depending on painstaking operations applied to micro volumes of solution. Furthermore, the high frequency detection of end-points provides an almost universal means of following the progress of titrations with ethylenediaminetetra-acetic acid: this is of special significance because of the great versatility of this reagent.

Titrations can be made directly, and the stoichiometric end-point established by means of the high frequency oscillator, or excess reagent can be added and the liberated ions can be subsequently titrated with a standard base. The direct titration is generally preferable and should normally be carried out in a buffered solution. Excellent end-points can be obtained by direct titrations of cobalt, nickel, copper (II), zinc, cadmium and lead, especially if the titrations are performed in the presence of acetate buffer. Manganese (II) can be titrated accurately provided the solution is buffered with acetate-acetic acid, and calcium can be determined by titration in the presence of phosphate buffer. Results obtained in the determination of magnesium, strontium and barium were erratic.

ACKNOWLEDGEMENT

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SUMMARY

The high frequency oscillator provides an excellent means of detecting the end-points of titrations performed with ethylenediaminetetraacetic acid or its salts. The determination of various divalent metals is reported, based on both direct and indirect titrations. Because of the great sensitivity of the method it is possible to determine cobalt, nickel, copper (II), zinc, cadmium, lead and manganese (II) in concentration ranges of 1/1000 to 1/6000*M*.

RÉSUMÉ

L'oscillateur à haute fréquence permet de déterminer avec précision les points finaux de titrations effectuées au moyen de l'acide éthylènediaminotétracétique ou de ses sels. La détermination de divers cations divalents est donnée, elle s'effectue par titration directe ou indirecte. Cette méthode est très sensible, on peut ainsi déterminer le cobalt, le nickel, le cuivre(II), le zinc, le cadmium, le plomb et le manganèse(II) en concentration 1/1000 et 1/6000*M*.

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ZUSAMMENFASSUNG

Der Hochfrequenzoszillator ermöglicht eine genaue Endpunktbestimmung für Titrationen, welche mit der Ethylendiaminotetraessigsäure oder ihren Salzen durchgeführt werden. Die Bestimmung verschiedener zweiwertiger Kationen wird beschrieben; sie wird durch direkte oder indirekte Titration ausgeführt. Diese Methode ist sehr empfindlich; man bestimmt auf diese Weise Kobalt, Nickel, Kupfer(II), Zink, Kadmium, Blei und Mangan(II) in Konzentrationen von 1/1000 und 1/6000*M*.

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DOSAGES COULOMÉTRIQUES À COURANT CONSTANT ET EN SOLUTION NON AGITÉE

par

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INTRODUCTION

L'utilisation de l'électron comme agent titrant constitue la base de diverses méthodes électrochimiques d'analyse. La quantité de réactif mise en oeuvre se calcule à partir de mesures d'intensité et de temps.

La *coulométrie*, particulièrement simple, est utilisable chaque fois que la réaction d'électrode est complète et spécifique.

La *coulométrie à courant constant* présente l'avantage de la plus grande simplicité opératoire. Dans ce cas, la courbe du potentiel de l'électrode en fonction du temps présente, après une durée T, une brusque montée, qui signale le terme du titrage.

La concentration cherchée C, en molécule-gramme par litre, s'exprime par

$$C = \frac{I.T}{nF.V} \quad \text{(I)}$$

où V est le volume de solution en l; I l'intensité imposée en A; T le temps total en sec; F le faraday exprimé en coulombs; et n le nombre d'électrons-g échangé par une mol.-g de la substance à doser.

La validité de la relation (I) peut être discutée à deux points de vue:

1) Les conditions expérimentales qui correspondent au saut de potentiel final sont celles de la potentiométrie sous courant constant. On sait[1,2] que cette méthode se caractérise par une erreur systématique par défaut. En effet, l'apparition du saut signifie que la réaction d'électrode devient insuffisante à consommer la totalité de l'intensité imposée, et non que cette réaction est terminée.

Il subsiste en solution une concentration résiduelle, qui dépend principalement de la densité du courant et du degré d'agitation. Dans chaque cas particulier, il est nécessaire de réaliser un compromis satisfaisant entre facteurs rapidité et précision (respectivement proportionnel et inversement proportionnel à la densité du courant).

2) L'électrode auxiliaire est le siège d'une réaction de dépolarisation dont les produits solubles sont susceptibles d'interférer. L'emploi de ponts de jonction ou

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de diaphragmes élimine cette source d'erreur, mais entraîne à son tour des risques de perte par diffusion ou migration, dont l'évaluation exacte est souvent difficile.

Il semble possible d'éliminer ces inconvénients si l'analyse est effectuée, non plus sur le volume total de solution, mais dans un espace restreint, localisé au voisinage immédiat de l'électrode.

Si les conditions expérimentales sont définies et réalisées de manière suffisamment stricte, le volume où se limite le dosage peut être évalué avec précision. Il dépend essentiellement des modalités de l'apport vers l'électrode, que l'on réduit aisément à la seule diffusion par addition d'un large excès d'électrolyte indifférent, et par utilisation de solutions non agitées.

COULOMÉTRIE EN RÉGIME TRANSITOIRE

Définition du volume équivalent

Supposons que l'électrolyse ait créé, au temps T, la répartition de la concentration c schématisée (Fig. 1) par la courbe en trait plein (x est la distance à l'électrode).

On peut concevoir une autre répartition de la concentration, purement fictive, mais équivalente au point de vue du bilan massique, où la solution serait entièrement appauvrie depuis l'électrode jusqu'à une distance δ à partir de laquelle la concentration reprendrait sa valeur initiale C (courbe en trait discontinu).

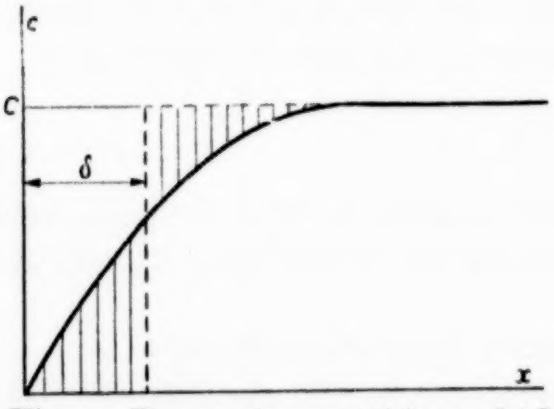

Fig. 1. Expression graphique de δ.

δ est choisi de telle sorte que les deux aires hachurées soient égales.

Le volume équivalent $\overline{V}$ vaut $S.\ \delta$ (S étant la surface de l'électrode en cm^2), ou encore:

$$\overline{V} = \frac{S}{C}\int_0^\infty (C - c)\,dx \quad (\mathrm{II})$$

La relation initiale (I) reste valable, à la condition d'y remplacer V par $\overline{V}$. La seule différence réside dans le fait que $\overline{V}$ ***n'est généralement pas une constante,*** mais dépend de certains facteurs dont il est nécessaire d'évaluer la fonction mathématique.

Ce calcul s'effectue en résolvant l'équation seconde de FICK, à l'aide de conditions-limites appropriées. La solution de cette équation permet de tirer la loi de variation de la concentration à l'électrode $c_{x=0} = \mathrm{f}(t)$. La fonction $E = \mathrm{f}(t)$ s'en déduit aisément. La valeur particulière de t qui correspond au saut de potentiel du virage permet finalement d'expliciter l'expression du volume équivalent.

Etat des concentrations durant l'électrolyse

On suppose que:
1) la solution n'est pas agitée;
2) elle est initialement homogène jusqu'à l'électrode;
3) la diffusion est le seul mode d'apport; elle s'effectue perpendiculairement à l'électrode supposée plane;
4) le volume de solution est suffisant pour qu'aucun obstacle ne perturbe l'extension de la couche de diffusion.

Aux premiers instants de l'électrolyse, le potentiel de l'électrode croît très rapidement, par élévation de sa charge capacitive, jusqu'à la valeur E_R, où la réaction coulométrique débute (intervalle $t_0 — t_1$. Fig. 3).

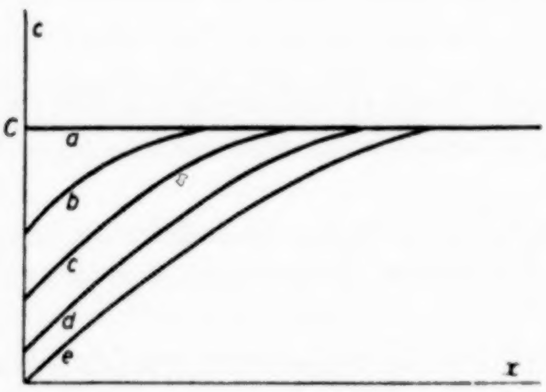

Fig. 2. Etat des concentrations.

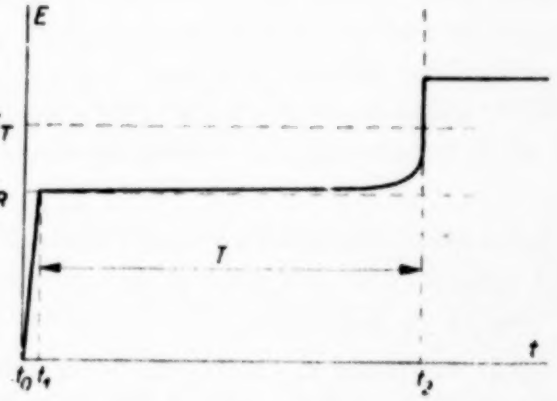

Fig. 3. Courbe de transition.

A partir de t_1, l'électrolyse s'effectue sous densité constante, c'est-à-dire, en terme de transfert de masse, à gradient constant à la surface de l'électrode;

$$\left(\frac{\delta c}{\delta x}\right)_{x=0} = C^{te} = \frac{I}{nF\,DS}$$ où D est le coefficient de diffusion de la particule dosée en cm^2 sec^{-1}.

Les courbes a, b, c, . . . (Fig. 2) schématisent l'état des concentrations après des intervalles de temps constants.

La résolution de l'équation seconde de FICK[3], à l'aide des hypothèses énoncées, conduit à l'expression:

$$c_{x=0} = C - \frac{2\,I}{nF\,S}\sqrt{\frac{t}{\pi D}} \quad \text{(III)}$$

Le temps de transition

Lorsque $c_{x=0}$ atteint une valeur suffisamment faible (temps t_2), la réaction de décharge à l'électrode ne peut plus s'effectuer à une vitesse suffisante. L'excès d'intensité imposée élève la charge capacitive de l'électrode jusqu'à atteindre le potentiel rédox d'une autre substance.

L'intervalle $t_2 - t_1$ constitue le ***temps de transition*** T de l'électrolyse.

Dans la plupart des cas, le temps de transition est atteint lorsque $c_{x=0} = 0$ *.

Dès lors,

$$C = \frac{2I}{nFS} \sqrt{\frac{T}{\pi D}} \quad \text{(IV)}$$

A partir de cette relation, on établit que le volume équivalent précédemment défini vaut:

$$V = \frac{S}{2} \sqrt{\pi D T} \quad \text{(V)}$$

Cette relation montre que pour une substance dosée et une électrode déterminée (D et S constants), ***le volume équivalent dépend uniquement de la durée de transition.***

La coulométrie réalisée sous intensité constante et en régime transitoire est, en fait, une coulométrie effectuée dans un volume de solution proportionnel à la racine du temps de transition.

Cette méthode se distingue de la coulométrie classique par sa très grande rapidité, due au faible volume titré. Elle en élimine tous les inconvénients précédemment cités.

PRINCIPE DES APPLICATIONS ANALYTIQUES

On peut envisager d'utiliser la relation (IV) en évaluant chacun de ses termes. Cette méthode absolue est d'un intérêt pratique limité, car ni la surface exacte de l'électrode, ni le coefficient de diffusion D, ne sont généralement connus avec une précision suffisante.

Comme en polarographie, il est beaucoup plus commode d'opérer par comparaison à l'aide d'une solution-étalon.

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* Les seules exceptions sont celles où la vitesse de la réaction est limitée à une valeur finie, non susceptible d'être augmentée par une élévation du potentiel de l'électrode (existence d'une étape chimique lente préalable à la décharge et non influencée par le potentiel, effets de répulsion électrostatique, adsorption de substances inhibitrices). T est alors atteint pour $c_{x=0} > 0$.

Dans ces cas, l'étude de la dépendance liant i à T fournit des indications quantitatives sur la cinétique de l'étape déterminante[1,5,6]. Ces comportements particuliers sont suffisamment peu fréquents pour que leur exposé détaillé soit utile dans le cadre de cette communication.

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Pour une substance à doser, une température et un milieu donnés, et si on utilise une électrode de géométrie invariable, (IV) peut s'écrire:

$$\frac{C}{I\sqrt{T}} = \text{constante} \quad \text{(V)}$$

Pour diverses concentrations C et une même intensité I, on a:

$$C = K\sqrt{T} \quad \text{(VI)}$$

L'évaluation de K est évitée par l'emploi d'une solution de référence de concentration C'

$$\frac{C}{C'} = \sqrt{\frac{T}{T'}} \quad \text{(VII)}$$

Pour effectuer un dosage par comparaison, il n'est donc nécessaire de connaître ni les valeurs de l'intensité imposée et de la température (elles doivent seulement rester constantes d'une expérience à l'autre), ni les caractéristiques géométriques de l'électrode utilisée, ni même la valeur absolue des temps de transition.

EFFETS CAPACITIFS

Les relations (V) et (VII) ne sont vérifiées que pour autant que toutes les conditions formulées précédemment sont effectivement réalisées. Il importe en particulier que, durant la transition, la densité de courant I_d consommée par la réaction d'électrolyse soit maintenue constante. Cette condition n'est jamais rigoureusement satisfaite du fait de l'existence d'une composante de charge capacitive $I_k = K.\mathrm{d}E/\mathrm{d}t$, d'autant plus importante en valeur absolue que la vitesse de variation du potentiel de l'électrode est grande.

Si I_m désigne l'intensité imposée,

$$I_d = I_m - K.\mathrm{d}E/\mathrm{d}t$$

Le terme capacitif tend à diminuer l'intensité effective I_d, c'est-à-dire à augmenter le temps nécessaire pour atteindre une valeur de potentiel déterminée. L'effet est le plus marqué dans la zone du potentiel de transition, où la variation $\mathrm{d}E/\mathrm{d}t$ est particulièrement importante (Fig. 4).

Pour une durée de transition déterminée, *l'interférence de la composante capacitive*, mesurée par le rapport I_k/I_d *est d'autant plus négligeable que* $I_d > I_k$, c'est-à-dire que *la concentration est élevée.*

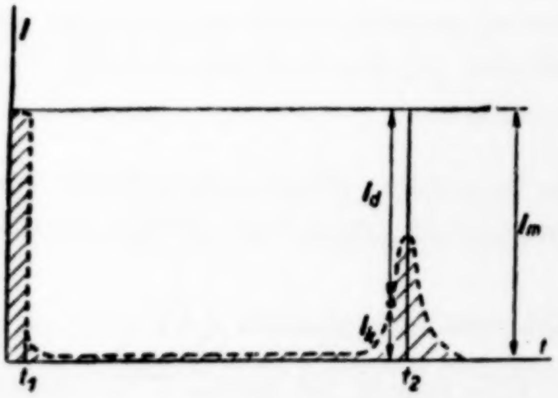

Fig. 4. Distribution du courant imposé.

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Pratiquement, pour des durées de transition de l'ordre de 0.2 seconde, l'effet est négligeable jusqu'à des concentrations d'environ $5 \cdot 10^{-4} N$.

Pour une concentration fixée et des intensités variables, et pour un même degré d'achèvement de la transition:

$$I_k/I_d = k/I_d T = k'/C \sqrt{T} = k''/\sqrt{T}$$

La composante capacitive est d'autant plus faible que la durée de transition est grande.

Il reste possible d'évaluer des concentrations de l'orde de $10^{-4} N$, pour des durées de transition de l'ordre de quelques secondes.

Pour des concentrations inférieures à $10^{-4} N$, il est nécessaire d'établir une courbe de calibrage $T = \mathrm{f}(C)$.

L'effet capacitif peut être éliminé si on impose un courant de la forme:

$$I_m = Cte + K.\mathrm{d}E/\mathrm{d}t \quad \text{(X)}$$

La composante corrective $K.\mathrm{d}E/\mathrm{d}t$ peut être imposée automatiquement à l'aide d'un circuit électronique différenciateur, dont le schéma de principe a été décrit ailleurs[4].

APPAREILLAGE

La méthode proposée n'est susceptible de présenter un intérêt pratique que si la détermination des durées de transition peut s'effectuer sans recourir à l'oscillographe à rayons cathodiques, dont l'emploi rendrait les manipulations relativement délicates, et le coût total de l'appareillage prohibitif.

A cet effet, deux ,,transitomètres" ont été construits. Ces appareils ont une double fonction: ils polarisent l'électrode sous une intensité constante ajustable et, simultanément, mesurent automatiquement la durée de transition à l'aide d'un dispositif chronométrique électronique. L'un a été destiné à étudier les possibilités analytiques offertes par les électrodes solides; l'autre utilise une électrode de mercure à surface contrôlée.

1. Le schéma général du premier des deux appareils (Fig. 5) comprend cinq circuits principaux qui seront sommairement décrits.

Alimentation générale Ⓐ

Elle fournit les tensions continues (150 V, 300 V, 250 V) et alternative (20 V) nécessaires.

Les tensions 150 V et 300 V sont stabilisées à l'aide de tubes-néon régulateurs.

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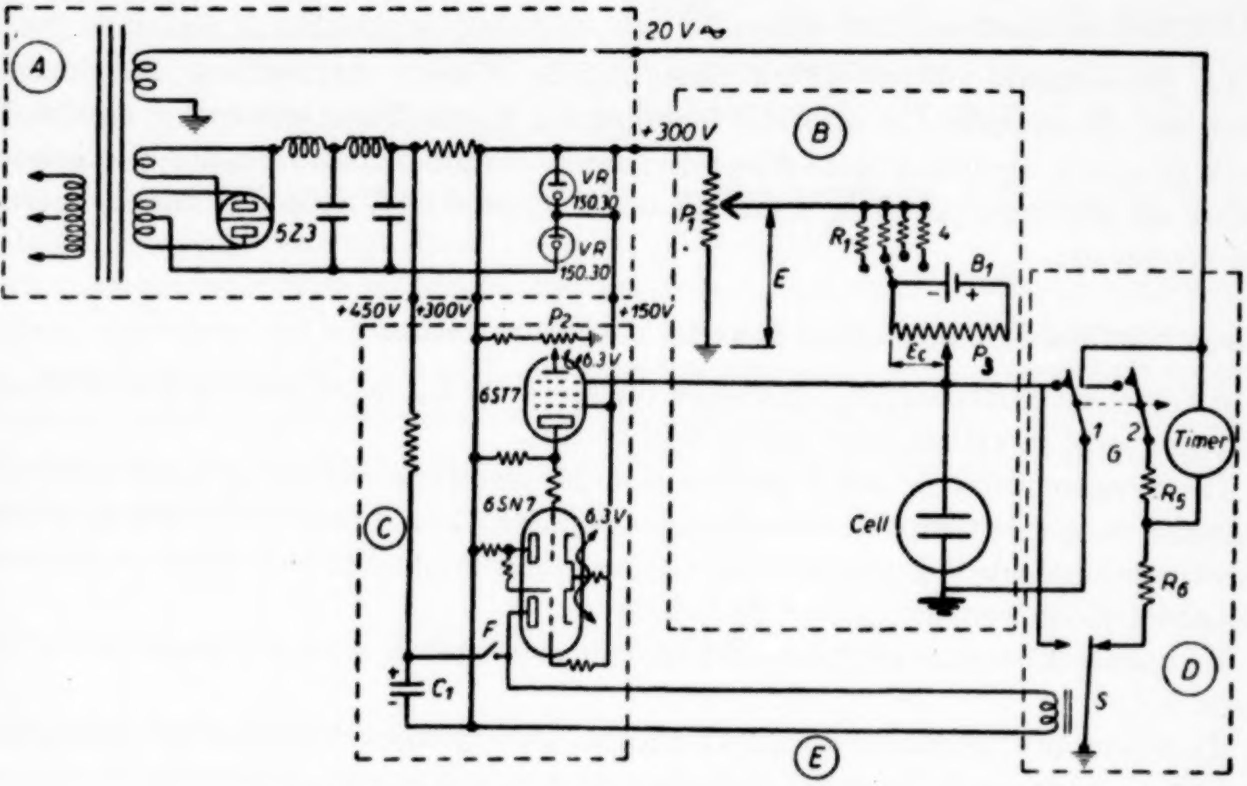

Fig. 5. Schéma électrique du transitomètre.

Circuit de polarisation Ⓑ

Il comprend un diviseur de tension P_1 et diverses résistances de charge calibrées R_{1-4}.

La force contreélectromotrice E_c développée par la cellule durant l'intervalle de transition dépend de la nature de l'ion dosé. Elle est compensée par le circuit potentiométrique auxiliaire B_1P_3.

La tension effective E-E_c est mesurée à l'aide d'un potentiomètre de mesure, d'une précision supérieure à 0.1 %.

La cellule est courtcircuitée en dehors des mesures. L'ouverture manuelle de la clé à rappel G, dans le sens de la flèche, a pour effet simultané:

1°) de forcer le courant imposé à travers la cellule (G_1),

2°) d'enclencher le chronomètre (G_2).

Relais électromécanique Ⓒ

Ce relais commande l'arrêt de chronomètre, au moment où le potentiel de l'électrode dépasse la valeur E_T choisie en fonction de la courbe potentiel-temps de la substance à doser (Fig. 3).

Il comprend un amplificateur à haute impédance d'entrée; son étage final, du type „trigger", bascule pour un potentiel d'entrée stable à moins d'un millivolt et ajusté par P_2. Il excite un inverseur mécanique polaire S à faible inertie, à deux positions stables.

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Mesure de T Ⓓ

Le chronomètre utilisé est un timer rapide ,,Cenco" permettant d'évaluer le centième de seconde. Cet appareil fonctionne à partir d'une tension de l'ordre de 20 V 50 cps. L'aiguille avance d'une division à chaque demi-alternance. Ce chronomètre est préexcité par R_5R_6 à une tension d'environ 15 V, afin d'éliminer l'inertie de démarrage.

Circuit de remise automatique dans les conditions initiales Ⓔ

A l'arrêt du chronomètre, l'opérateur ramène la clé G à sa position initiale, et courtcircuite ainsi la cellule avec un certain retard.

Il est cependant utile que la polarisation de l'électrode soit interrompue instantanément dès que le temps de transition est dépassé. On réduit ainsi la consommation électrochimique de la substance dosée à une valeur minimum, en évitant en outre un éventuel recouvrement gazeux de l'électrode.

La cellule de mesure est à cet effet courtcircuitée par le second contact de l'inverseur S.

Le retour aux conditions initiales s'effectue en déchargeant, par la clé F, le condensateur C_1 à travers la bobine d'excitation de S, ce qui inverse la position du contact basculant.

2. Le second appareil réalisé est basé sur un principe analogue. Il présente les particularités suivantes:

A. Un circuit auxiliaire contrôle la surface de l'électrode de mercure faisant office de cathode. Le schéma de principe, basé sur l'utilisation d'une électrode à goutte à cadence très lente et l'emploi d'un circuit retardateur qui fait débuter le régime d'électrolyse à un stade constamment identique de la surface cathodique, a déjà été décrit[4].

B. L'évaluation de T s'effectue en mesurant le potentiel pris par une capacité à haut isolement, chargée à courant constant durant l'intervalle de transition. Cette mesure est réalisée à l'aide d'un pH-mètre et d'un circuit potentiométrique diviseur.

Précision sur la mesure de T

Dans le premier appareil décrit, la précision est limitée par le fonctionnement discontinu du chronomètre. Chaque mesure de temps est affectée d'une incertitude de ± 0.02 seconde.

Cependant, du fait qu'il n'y a pas de synchronisme entre les limites de l'intervalle de transition et la phase de la tension alternative qui excite le chronomètre, la répétition des mesures réduit l'erreur, celle-ci étant d'ordre statistique.

Le second appareil permet des mesures de temps plus précises.

A l'aide d'expériences effectuées en remplaçant la cellule d'électrolyse par un condensateur, il est possible de mettre en évidence deux causes d'erreur:

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a) une erreur systématique, par excès, due à l'inertie du relais de fin de transition. Cette erreur, de l'ordre de 0.5 milli seconde, est compensée électriquement en retardant d'un intervalle équivalent le début de l'électrolyse par rapport au début de la charge de la capacité de mesure.

b) des fluctuations irrégulières, liées à l'irreproductibilité du basculement des relais. Leur écart-type est d'environ 0.02 milliseconde.

La comparaison entre les écarts observés de part et d'autre, montre que la mesure potentiométrique du temps de transition est environ cent fois plus précise.

Cependant, l'appareil utilisant le chronomètre électromécanique possède un encombrement réduit et une simplicité de fonctionnement tels que son emploi est utile chaque fois que les durées de transition peuvent être portées sans inconvénient à plusieurs secondes.

RÉSULTATS EXPÉRIMENTAUX

Emploi d'une électrode solide

Divers dosages ont été effectués à l'aide d'une électrode de platine brillant, constituée par un fil de quelques millimètres de longueur soudé à l'extrémité d'un tube de verre, et n'ayant subi d'autre traitement superficiel qu'un décapage à l'acide nitrique $6N$.

Les ions Fe^{+2}, Fe^{+3}, $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$, Ag^+, MnO_4^- sont dosables à des concentrations supérieures à $5 \cdot 10^{-4}N$, avec une précision de l'ordre du pourcent. La méthode est inapplicable à la détermination des ions Ce^{+4} et Ti^{+3}, dont la réaction de décharge ne donne pas de courbe de transition suffisamment définie.

Les résultats relatifs au dosage de l'ion ferricyanhydrique seront seuls reproduits ici, à titre d'exemple.

Etude de la réaction

On utilise une solution de composition $[Fe(CN)_6]^{-3}$ $5 \cdot 10^{-3}M$, KClM et $[Fe(CN)_6]^{-4}$ $10^{-3}M$.

L'addition de ferrocyanure fixe le potentiel de l'anode de pH et évite l'emploi d'une électrode de référence.

1. La courbe potentiel-temps, établie point par point (Fig. 6) permet de déterminer la valeur du potentiel de fin de transition la plus favorable (—0.15 V).

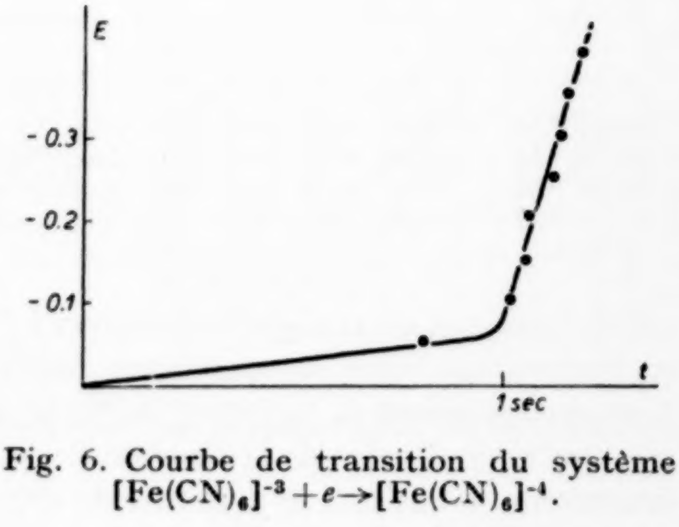

Fig. 6. Courbe de transition du système $[Fe(CN)_6]^{-3} + e \rightarrow [Fe(CN)_6]^{-4}$.

2. La relation $I\sqrt{T} = f(I)$ donne d'utiles indications sur la réversibilité de la réaction d'électrode (Tableau I).

TABLEAU I

I (a)	T en sec (moyenne de 10 mesures)	$I\sqrt{T}$ (a)
0.5	3.10	0.88
1.0	0.77	0.88
1.5	0.33	0.86
2.0	0.19	0.87

(a): en unités arbitraires

Ces résultats indiquent que l'expression $I\sqrt{T}$ est substantiellement indépendante de I. La réaction d'électrode est par conséquent rapide, et utilisable à des fins analytiques.

Etude du dosage

Elle se ramène à celle de la fonction $I\sqrt{T} = f(C)$.

Diverses solutions de concentration connue sont préparées à partir de deux solutions-mères ayant respectivement les compositions:

A- $[Fe(CN)_6]^{-3}$ $10^{-2}M$
$[Fe(CN)_6]^{-4}$ $10^{-2}M$
KCl $2M$
B- KCl $2M$

Le Tableau II est relatif à des mesures effectuées sous une intensité de 1.00 mA.

TABLEAU II

C	T (centisec)	$I\sqrt{T}$	$\frac{I\sqrt{T}}{C}$
$2.00 \cdot 10^{-3}M$	150, 152, 151, 152, 154, 152, 152, 151, 153, 152	12.3	$6.15 \cdot 10^3$
$1.82 \cdot 10^{-3}M$	126, 128, 126, 126, 124, 125, 125, 126, 126, 125	11.2	$6.15 \cdot 10^3$
$1.67 \cdot 10^{-3}M$	105, 104, 103, 105, 105, 107, 105, 104, 105, 104	10.2	$6.14 \cdot 10^3$
$1.54 \cdot 10^{-3}M$	90, 92, 93, 92, 92, 90, 92, 92, 91, 93	9.5	$6.21 \cdot 10^3$

Ces chiffres montrent que l'expression $I\sqrt{T}$ est proportionnelle à la concentration en ferricyanure, avec un écart-type inférieur à 0.5%. Cette bonne précision est due principalement au fait que l'électrode n'est polarisée que durant des intervalles très courts, de l'ordre de la seconde, le courant de charge étant automatiquement interrompu avant que le potentiel de dégagement de l'hydrogène ne soit atteint.

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Emploi d'une électrode de mercure

En principe, toute substance dosable au polarographe peut être déterminée. La seule exception est celle des ions qui sont susceptibles d'oxyder spontanément le mercure ($S_2O_8^{-2}$, $[Fe(CN)_6]^{-3}$, etc.) et dont l'onde polarographique se développe dès le début du polarogramme.

Les mesures suivantes sont relatives au dosage du cadmium en tampon ammoniacal (Tableau III). Les solutions étudiées ont la composition:

A: $CdSO_4$ 0.800 $10^{-2}M$
B: 0.880 ,,
C: 0.960 ,,
D: 1.040 ,,

dans un électrolyte-support: NH_4Cl $1M$
NH_4OH $1M$
SO_3Na_2 $10^{-1}M$
Gélatine 0.0001%

les conditions expérimentales étant:

température: 25° C + 0.1
surface de la goutte: 2.27 mm^2
intensité imposée: 0.2488 mA
potentiel de transition: —1.30 V/E.N.C.

Il a été tenu compte de la force contreélectromotrice de la cellule (0.80 V) de la résistance du capillaire (172 ohms) et du retard d'ouverture du relais de rupture (0.52 msec).

TABLEAU III

Solution	T (millisec)					T moyen	Ecart type	$I\sqrt{T}$ (mA. msec. $\frac{1}{2}$)	$\frac{I\sqrt{T}}{C}$ (mA. msec. $\frac{1}{2}$ mole^{-1})
A	383.3	383.3	379.7	379.1	379.1	379.7	0.6	4.848	606.0
B	456.8	465.2	460.9	462.7	460.9	463.1	2.4	5.354	608.4
C	547.1	548.5	547.3	548.0	547.1	547.6	0.2	5.821	606.4
D	636.8	638.0	640.5	639.3	639.3	638.8	1.4	6.288	604.6
						Moyenne	:		606.4
						Ecart-type	:		1.5
						Ec.-type%	:		0.25

La constance de $\frac{I\sqrt{T}}{C}$ est d'autant meilleure que le potentiel de fin de transition choisi est moins négatif:

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E_T	$\frac{I\sqrt{T}}{C}$ (moyenne des 4 solutions)	Ecart-type en %
—1.50	609.8	0.40
—1.30	606.4	0.25
—1.10	602.5	0.20

D'une manière générale, il est possible d'effectuer des dosages avec une précision de l'ordre de 0.2 à 0.3%, à la condition de pouvoir disposer de solutions relativement concentrées (de concentration supérieure à $5 \cdot 10^{-3} N$).

CONCLUSIONS GÉNÉRALES

L'examen critique d'un grand nombre de mesures systématiques, analogues à celles décrites, permet de définir les caractéristiques de la méthode en fonction des principaux critères analytiques.

La *rapidité* des mesures, de l'ordre de 20 secondes, est considérablement plus élevée que celle des mesures polarographiques et coulométriques.

Cet avantage n'est cependant réel que pour des dosages effectués en série, où le temps consacré aux manipulations préliminaires est négligeable vis-à-vis de la durée d'utilisation totale.

La *précision* est de l'ordre du millième pour des solutions environ centinormales, l'ion dosé étant déchargé réversiblement.

Les solutions millinormales peuvent être déterminées à moins de 1%. Pour des solutions plus diluées, il y a intérêt à utiliser le polarographe.

La *sensibilité* est limitée par l'existence d'une capacité d'électrode. Elle est inférieure à celle des méthodes polarographique et coulométrique. Des concentrations inférieures à environ $3 \cdot 10^{-4} N$ ne sont plus évaluables avec une précision suffisante.

La *spécificité* est équivalente à celle du polarographe. Le choix du potentiel de transition E_T permet de séparer les divers ions en présence, si leurs potentiels de décharge sont écartés de plus de 0.2 V.

Les dosages simultanés sont possibles, soit par calcul direct à partir des durées de transition successives[7], soit en recourant à la technique de prépolarisation.

Le *domaine d'application* n'est limité ni par l'utilisation d'un type déterminé d'électrode, ni par la nécessité de réaliser un état stable en régime stationnaire.

A ce point de vue, l'emploi d'une électrode solide semble particulièrement intéressant. Dans le domaine des concentrations moyennes, la précision du dosage est très supérieure à celle atteinte avec une électrode tournante. Etant donné l'intervalle de polarisation très bref, l'état de surface reste pratiquement inaltéré, et des réactions d'électrodéposition peuvent être utilisées. En outre, toutes les fluctuations de nature hydrodynamique sont éliminées, l'électrolyse s'effectuant dans tous les cas en solution non agitée.

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RÉSUMÉ

La mesure précise des temps de transition observables lors d'électrolyses effectuées sous courant constant et en solutions non agitées, peut être utilisée à des fins analytiques.

On décrit un appareillage spécialement adapté à ce but.

Quelques exemples d'application illustrent les possibilités de la méthode et ses principales caractéristiques.

Dans des conditions favorables, les déterminations peuvent s'effectuer en moins d'une minute, avec une précision de l'ordre de 0.2 %.

SUMMARY

Accurate evalution of "transition times" occurring during constant current electrolysis in non-stirred media may be used analytically. An apparatus has been devised for such a purpose.

The method has been applied to various practical problems and stress is laid on its potentialities and main features.

Under favourable conditions, determinations are performed in less than one minute, with an accuracy of about 0.2%.

ZUSAMMENFASSUNG

Die genaue Messung der Transitionszeiten, welche man bei Elektrolyse unter konstantem, Stromdurchfluss und ohne Rührung beobachtet, kann zu analytischen Zwecken verwendet werden.

Es wird ein Apparat beschrieben, der speziell für eine solche Anwendung gebaut wurde.

Einige Beispiele illustrieren die Möglichkeiten und besonderen Eigenschaften dieser Methode.

Unter günstigen Bedingungen können die Bestimmungen in weniger als einer Minute mit einer Genauigkeit von ungefähr 0.2% ausgeführt werden.

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OXIDATION WITH ALKALINE PERMANGANATE USING FORMIC ACID FOR THE BACK-TITRATION

II. POTENTIOMETRIC DETERMINATION OF CHROMIUM

by

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The methods usually employed for the determination of chromium depend mainly on its primary oxidation to chromate. This latter product is then either determined gravimetrically by precipitation as lead or barium chromate, or potentiometrically as silver chromate[1]. Hexavalent chromium is also determined volumetrically or potentiometrically with a standard solution of a reducing agent such as arsenite[2], ferrous iron[3], stannous chloride[4] or chromous chloride[2]. Another method depends upon the oxidation of chromium with an excess ceric sulphate[5] solution, followed by back-titrating the excess of oxidant with nitrite or oxalic acid. Alternatively the excess oxidant may be destroyed and the chromate solution determined as usual. The only method capable of determining trivalent chromium by direct potentiometric titration was devised by HAHN[6] who used potassium ferricyanide as an oxidant in strong alkaline solutions.

In this communication a method which depends upon oxidation of trivalent chromium with potassium permanganate in alkaline solution is described.

EXPERIMENTAL

Preparation and standardization of solutions

a) Potassium permanganate solutions were prepared and standardized as given before[7].

b) Chromic solutions were prepared by dissolving chromic chloride in twice distilled water or in a solution of dilute hydrochloric acid ($\sim 0.2N$) followed by filtration through a 1G4 sintered glass crucible. The chromium content of these solutions was determined by oxidation to the hexavalent condition, followed by titration with a standard ferrous solution. Oxidation was effected by potassium permanganate in the presence or absence of silver ions[8].

The working conditions are the same as described previously[7]. In the titration of $KMnO_4$ with Cr^{+3} solutions, addition of the titrant was made dropwise, in order to minimize as far as possible, reduction of $KMnO_4$ to MnO_2 in the presence of Ba^{+2} ions.

RESULTS

Undoubtedly the oxidation of trivalent chromium to the hexavalent state depends upon its primary transformation to chromite, chromium hydroxide being amphoteric, dissolves when freshly precipitated in alkali hydroxide. From the theoretical point of view, oxidation of chromite with alkaline permanganate can be effected quantitatively. The equilibrium constant of the reactions:

(1) $Cr^{+3} + Mn^{+7} \rightarrow Cr^{+6} + Mn^{+4}$ and
(2) $Cr^{+3} + 3\ Mn^{+7} \rightarrow Cr^{+6} + 3\ Mn^{+6}$

which are supposed to occur in alkaline medium, as calculated from the redox potentials of the system involved ($E_{CrO_4^{-2}/CrO_2^{-}} = -0.13$ volt, $E_{MnO_4^{-}/MnO_2} = 0.588$ volt and $E_{MnO_4^{-}/MnO_4^{-2}} = 0.564$ volt)[9] together with the number of Faradays necessary for their completion (*i.e.* 3), amounts to $3.1 \cdot 10^{-37}$ and $5.15 \cdot 10^{-36}$ for reactions (a) and (b) respectively. The degrees of completion calculated with the help of these K values and the valency changes of the ions participating in the reactions amount also to $8.23 \cdot 10^{-7}$ and $1.51 \cdot 10^{-9}$ for both reactions.

However as may be seen below, the process of oxidation was beset with several difficulties especially in the direct oxidation of chromite with permanganate.

Reduction of potassium permanganate with trivalent chromium

(A) The most accurate results given by the method described in this paper are those obtained by titrating potassium permanganate with the chromic solutions in the presence of barium ions. The accuracy is, as a rule, not bad in the case of the more concentrated chromium solutions used, *viz.* $0.174N$ and $0.159N$ when the permanganate is made 0.8-1.5N with respect to NaOH. Under these conditions, the errors vary from -0.27 to $+0.27$, in the presence of Ba^{+2} ions equivalent or $1^1/_2$ equivalent to the manganate and chromate formed in the reaction. At lower

TABLE I

TITRATION OF 25 ml $0.126N$ $KMnO_4$ WITH $0.174N$ Cr^{+3} IN THE PRESENCE OF Ba^{+2} IONS

Normality of NaOH	Vol of 5% $Ba(NO_3)_2$	Max. inflec. per 0.1 ml Cr^{+3}	Cr Equiv. to $KMnO_4$	Cr consumed in titration	error %
0.5N	10 ml	194 mv	10.920 mg	11.252 mg	3.04
0.75	10 ,,	200 ,,	10.920 ,,	10.980 ,,	0.55
0.8	10 ,,	250 ,,	10.920 ,,	10.950 ,,	0.27
1.0	10 ,,	240 ,,	10.920 ,,	10.890 ,,	—0.27
1.0	7 ,,	217 ,,	10.920 ,,	10.935 ,,	0.14
1.5	10 ,,	109 ,,	10.920 ,,	10.950 ,,	0.27
1.7	5 ,,	142 ,,	10.920 ,,	11.040 ,,	1.10
2.0	10 ,,	161 ,,	10.920 ,,	10.498 ,,	—3.86

and higher alkalinities than this limit, considerable errors are observed, apparently due to the same causes as previously stated[10]. When the chromium solution is acidified with 0.1*N* HCl, less accurate results are obtained especially when the solution is diluted twofold. In this latter case the concentration of Ba^{+2} ions affect the results to a considerable extent. When 7 ml of 5% $Ba(NO_3)_2$ (containing Ba^{+2} ions equivalent to the MnO_4^{-2} and CrO_4^{-2} produced in the reaction) are used, good results are obtained, but not on using 5 or 10 ml of the Ba^{+2} solution. The late end-points attained in the presence of small amounts of Ba^{+2} ions are apparently due to partial reduction to MnO_2.

When the chromium solution was made 0.5*N* with respect to HCl the end-point was attained late with an error amounting to 4%. On using a 0.0339*N* Cr^{+3} solution, reasonable results were only obtained in the presence of the equivalent amount of Ba^{+2} ions. With more dilute solutions considerable errors were observed.

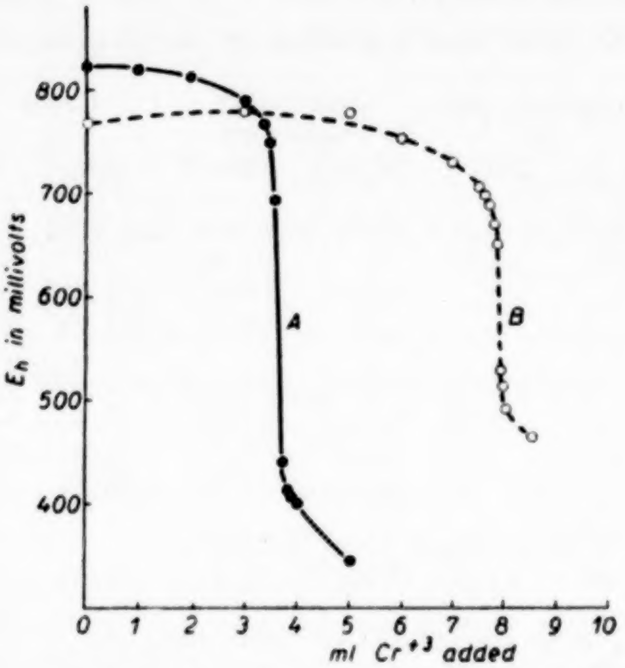
TABLE II

TITRATION OF $KMnO_4$ WITH Cr^{+3} SOLUTION IN PRESENCE OF Ba^{+2} IONS AND 1*N* NaOH

Acidity of Cr^{+3} solution	Volume of 5% $Ba(NO_3)_2$	Max. inflec. per 0.1 ml Cr^{+3}	mg Cr equiv. to $KMnO_4$	mg Cr consumed in titration	Error %
25 ml 0.1249*N* $KMnO_4$ titrated with 0.159*N* Cr^{+3} solution:					
0.1*N*	10 ml	195mv	10.821	10.780	—0.38
,,	,,	180 ,,	,,	10.969	—0.51
25 ml 0.1249*N* $KMnO_4$ titrated with 0.0795*N* Cr^{+3} solution:					
0.1*N*	10 ml	120 mv	10.821	10.702	—1.10
,,	5	30 ,,	,,	10.983	1.5
,,	7	119 ,,	,,	10.807	—0.13
0.5	7	82 ,,	,,	11.254	4.00
5 ml 0.1235*N* $KMnO_4$ titrated with 0.0339*N* Cr^{+3} solution:					
0.02	2	158 mv	2.275	2.170	—3.85
,,	1.5	135 ,,	,,	2.245	—0.54
10 ml 0.1249*N* $KMnO_4$ titrated with 0.0159*N* Cr^{+3} solution:					
0.1	4	70 mv	4.328	4.172	—3.8
25 ml 0.02499*N* $KMnO_4$ titrated with 0.0159*N* Cr^{+3} solution:					
0.1	1.5	103 mv	2.164	2.203	1.8

The reactions occurring under these conditions were such that the equilibria were attained after 1-2 min at the beginning of the titration and after 5 min at the end-point. The titration curves (Fig. 1 A and B) are characterized by sharp breaks in the region of the end-point varying from 250-120 mv per 0.1 ml of the chromium solution added.

(B) In the absence of barium ions, reduction proceeds primarily to manganate which passes then to manganese dioxide.



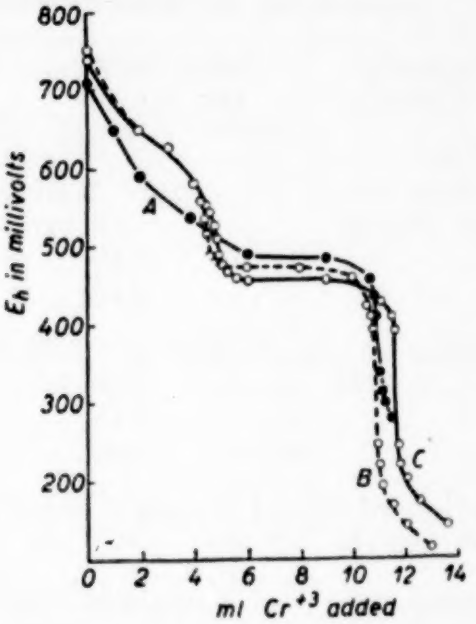


Fig. 1. A) Titration of 25 ml 0.126N $KMnO_4$ in 0.8N NaOH with 0.174N Cr^{+3} soln.
B) Titration of 25 ml 0.1249N $KMnO_4$ in 1N NaOH with 0.0795N Cr^{+3} soln.

Fig. 2 A) Titration of 25 ml 0.126N $KMnO_4$ in 0.5N NaOH with 0.174N Cr^{+3} soln.
C) Titration of 25 ml 0.126N $KMnO_4$ in 1.5N NaOH with 0.174N Cr^{+3} soln.
B) Titration of 25 ml 0.1249N $KMnO_4$ in 1.5N NaOH with 0.159N Cr^{+3} (acidity 0.1N HCl).

On titrating 0.1261N $KMnO_4$ with 0.174N Cr^{+3} solution, in the presence of 0.5N NaOH, inflection at the end-point of the manganate state is very poor. The second inflection occurring at the MnO_2 stage is quite distinct and occurs 0.8% late (curve A, Fig. 2). As the alkali concentration is raised to 1.5N NaOH the first inflection (at manganate) becomes somewhat defined but occurs 25% later than the theoretical value, possibly owing to the fact that the alkalinity is not quite sufficient to prevent reduction of $KMnO_4$ to MnO_2, and perhaps to the strong reducing power of the CrO_4^{-2}/CrO_2^- system ($E_0(OH) = -0.13$ volt[8]). Indeed brown particles were observed floating in the solution before the occurrence of the inflection. The inflection at the manganese dioxide state is sharper than in the presence of 0.5N NaOH, and the error is only — 0.1% (*cf.* curve B Fig. 2). The same phenomena manifest themselves when the solution is made 2N with respect to NaOH, except for the fact that the manganate state occurs only 15% later than the theoretical value.

When an acidified chromium solution was used, the errors were larger and the end-points were reached earlier possibly owing to partial decomposition of $KMnO_4$, catalysed by the considerable amount of MnO_2 formed primarily in the reaction, than in the case of the non-acidified solutions.

TABLE III

REDUCTION OF $KMnO_4$ WITH Cr^{+3} IN THE ABSENCE OF Ba^{+2} IONS

Alkalinity of $KMnO_4$	Max. inflec. per 0.1 ml		End-point calc. ml		End-point found ml		Error %	
	Mn^{+6}	Mn^{+4}	Mn^{+6}	Mn^{+4}	Mn^{+6}	Mn^{+4}	Mn^{+6}	Mn^{+4}
Titration of 25 ml 0.126N $KMnO_4$ with 0.1740N Cr^{+3} solution (no acid)								
0.5N NaOH	—	78 mv	3.62	10.86	—	10.95	—	0.81
1.5 ,,	24 mv	146 ,,	,,	,,	4.52	10.87	24.86	0.09
2 ,,	37 ,,	148 ,,	,,	,,	4.17	10.85	15.19	0.09
Titration of 25 ml 0.1249N $KMnO_4$ with 0.1590N Cr^{+3} solution in 0.2N HCl								
1N NaOH	19 mv	160 mv	3.93	11.79	5.64	11.77	38.39	0.13
1.5 ,,	21 ,,	145 ,,	,,	,,	4.95	11.67	25.95	1.03
2.5 ,,	53 ,,	144 ,,	,,	,,	4.41	11.65	12.21	1.19
Titration of 25 ml 0.1249N $KMnO_4$ with 0.0795N Cr^{+3} solution								
2.5N NaOH	17 mv	103 mv	7.86	23.58	8.65	23.25	10.05	1.4
Titration of 25 ml 0.02498N $KMnO_4$ with 0.0159N Cr^{+3} solution								
2.5N NaOH	9 mv	65 mv	7.86	23.58	7.84	23.04	0.26	2.3

Oxidation of trivalent chromium with permanganate and back-titrating of excess $KMnO_4$ with formic acid[7]

In the titration of permanganate with chromic salt solutions, good results were only obtained when the Cr^{+3} solution was 0.178N to 0.0339N, but not in the case of the more dilute solutions. It was deemed necessary to find out if amounts of chromium smaller than 2 mg could be determined with reasonable accuracy by mixing a given volume of the chromic solution with excess $KMnO_4$ in the presence of the appropriate alkali concentration, and then titrating excess $KMnO_4$ with formic acid[7]. The solution to be titrated with the latter reagent will contain a mixture of MnO_4^- and CrO_4^{-2} ions, both of which are capable of reduction by formate, as may be gathered from the redox potential values of these systems ($E_{HCO_2^-/CO_3^{-2}} = -1.01$ volt[11], $E_{CrO_4^{-2}/CrO_2^-} = -0.13$ and $MnO_4^-/MnO_4^{-2} = 0.564$). Although the difference in potential between the MnO_4^-/MnO_4^{-2} and the CrO_4^{-2}/CrO_2^- system in alkaline media amounting to 0.694 volt, permits reduction of any permanganate present without the interference of chromate as found experimentally, we precipitated all chromate as $BaCrO_4$ (by mixing $KMnO_4$ with Ba^{+2} ions before the addition of the Cr^{+3} solution). For the determination of chromium, known volumes of the chromic solutions were mixed with excess of $KMnO_4$, after making the latter solution either 2.5N with respect to NaOH in the absence of Ba^{+2} ions, or 1N if Ba^{+2} ions were present. Addition of the chromium solution was made dropwise, while continuously stirring, in order to prevent reduction of $KMnO_4$ to MnO_2. As may be seen from the results shown in Table IV, small quantities of chromium (as low as 0.6 milligrams) can be determined with an accuracy of 0.68%. On using 0.0159*N* Cr^{+3} solution, the error becomes appreciable amounting to $\sim$ 1.5% when the amount of Cr estimated is 276 γ.

TABLE IV

Volume and normality of $KMnO_4$	Volume and normality of Cr^{+3} soln.	Normality of formic acid used	mg Cr added	mg Cr found	Error %
50 ml 0.1249*N* (No Ba^{+2} ions)*	5 ml 0.159*N*	0.0637*N*	13.783	13.735	—0.35
(Ba^{+2} ")†	"	"	"	13.725	—0.42
" "	3 ml "	"	8.270	8.243	—0.33
" "	1 ml "	"	2.757	2.751	—0.27
25 ml 0.1203*N*	5 ml 0.0795*N*	0.0159*N*	6.891	6.880	—0.16
"	3 ml "	0.0637*N*	4.135	4.149	—0.34
"	1 ml "	"	1.378	1.386	0.44
5 ml 0.1235*N*	1 ml 0.0339*N*	0.02064*N*	0.587	0.0583	—0.68
50 ml 0.01249*N* $KMnO_4$ in 0.7*N* NaOH	1 ml 0.0159*N*	0.0159*N*	0.276	0.280	1.45

* Alkalinity 2.5*N* NaOH, † Alkalinity 1*N* NaOH.

Another reductant which may be used in the titration of excess permanganate is bivalent lead solution[10]. It possesses the advantage of being capable of reducing only MnO_4^- and not CrO_4^{-2} ions. Mixtures of permanganate and chromate were prepared, and the solutions titrated in presence of 2.5*N* NaOH with bivalent lead solution. The results obtained and which are shown in Table V indicate that quantitative reduction of permanganate can be effected if its concentration is at least double the chromate present. Better results are obtained when Ba^{+2} ions sufficient to precipitate the chromate are added and the titration is performed in presence of 1*N* NaOH.

TABLE V

TITRATION OF $KMnO_4$ — K_2CrO_4 MIXTURE WITH Pb^{+2} SOLUTION

Alkali concentration	Molarity of $KMnO_4$	Molarity of K_2CrO_4	Normality of Pb^{+2}	mg Pb equiv. to $KMnO_4$	mg Pb consumed in titration	Error %
2.5*N* NaOH (no Ba^{+2} ions)	0.0130	0.0714	0.0778	47.396	51.183	7.99
"	0.0152	0.0417	"	"	48.845	3.06
"	0.0163	0.0268	"	"	48.126	1.54
"	0.0169	0.0185	"	"	47.879	1.02
"	0.0176	0.0096	"	"	47.652	0.54
1*N* NaOH (Ba^{+2} ions)	0.0204	0.0417	0.1003	63.389	63.598	0.33

References p. 100

Oxidation of trivalent chromium with permanganate

Although the equilibrium constant and the degree of completion of reaction (1) page 93, permits quantitative oxidation of Cr^{+3} with MnO_4^-, the results obtained were associated with considerable errors, amounting in some cases to 16%. This is not the only disadvantage in the process, for the reaction proceeds so slowly that it needs ∿ 15 min at the beginning of the titration and 40 min near the end-point for the attainment of equilibrium. A vast number of experiments was made both in order to accelerate the reaction and to decrease the errors observed.

The catalysts tried to minimize the time of equilibrium were sodium chloride, Tl^{+3}, Fe^{+3}, Ag^+, Cu^{+2}, Ni^{+2}, Au^{+3} and Pt^{+4}. From these, the best catalysts are sodium chloride, Ag^+, Fe^{+3} and Tl^{+3}. In the case of 10% NaCl, the time was reduced to 3-5 min at the beginning, but the reaction slows near the end-point so that it still needed about 30 min for the addition just before the end-point. In the case where thallic or ferric salts were used alone (10-20 drops of a 0.10*N* solution), the reaction was not much accelerated. In the presence of these salts, together with sodium chloride, the reaction velocity was appreciably increased so that only 10 min in the case of Tl^{+3} and 7 min in the case of Fe^{+3} salts, were needed in the region of the end-point.

As may be visualized from the results shown in Table VI, the accuracy is much affected by the alkalinity, the rate of addition of permanganate solution and the prevailing gaseous atmosphere. In the presence of NaCl in aerated solutions, the best results (error 6.6 %) are obtained when the alkalinity of the solution is 0.1*N*. The error decreases to 4.7% when the reaction is carried out in an atmosphere of nitrogen.

The low results obtained are apparently due to the partial oxidation of chromite with atmospheric oxygen. Chromite, although stable in air[6], is not apparently so in the presence of oxides of manganese. That this is the case, is signified from the better results obtained on minimizing the time of experiment by adding large volumes of the titrant at a time. In conformity with this fact when 95% of the calculated volume of permanganate is added at the beginning, the end-point is reached only 0.5% early.

It was thought at first that, owing to the strong reducing power of the Cr^{+3}/Cr^{+6} system in alkaline solutions ($E_0(OH) = -0.13$ volt), the early end-point might be due to the reduction of $KMnO_4$ to Mn_2O_3. This then undergoes oxidation with the permanganate added to yield MnO_2, a process which is time-consuming, as it involves the oxidation of a solid product. However, by adding the volumes of $KMnO_4$ necessary for the end-point, on the basis of its reduction to Mn_2O_3, (75 % of the volume calculated on the basis of MnO_2) the chromate found was only slightly higher than corresponding to 75 % of the chromium present. This indicates that the reduction of $KMnO_4$ yields only MnO_2, and the slightly higher chromate concentration is brought about by the catalytic oxidation of chromite through atmospheric oxygen.

References p. 100

TABLE VI

TITRATION OF CHROMITE WITH $KMnO_4$ USING NaCl AS CATALYST

Rate of adding $KMnO_4$	Alkalinity of chromite	Theoret. vol. of $KMnO_4$	Max. inflec. per 0.1 ml $KMnO_4$	mg Cr present	mg Cr found	Error %
5 ml 0.159N Cr^{+3} as chromite diluted to 50 ml titrated with 0.1249N $KMnO_4$						
$KMnO_4$ added						
2 ml a time	—	10.6	43 mv	13.783	12.625	—8.4
	0.1N NaOH	„	93 „	„	12.873	—6.6
„	0.5N „	„	80 „	„	11.578	—16.0
„	1.0N „	„	100 „	„	„	—16.0
9.4 ml $KMnO_4$ added first	0.1N „	„	129 „	„	13.397	— 2.8
10 ml „	„ „	„	110 „	„	13.718	— 0.47
20 ml 0.00318N Cr^{+3} as chromite titrated with 0.01249N $KMnO_4$:						
$KMnO_4$ added						
2 ml a time	0.1N NaOH	8.5	33 mv	1.103	0.960	—12.8
7.5 ml $KMnO_4$ added first	„ „	„	„ „	„	1.056	— 4.18
10 ml 0.00636N Cr^{+3} as chromite titrated with 0.01249N $KMnO_4$:						
8.2 ml $KMnO_4$ added first	0.1N NaOH	8.5	95 mv	1.103	1.113	0.91

The results obtained by performing the reaction in the presence of nitrogen, confirms the idea of catalytic oxidation of chromite, as the errors observed are lower than those obtained in air (see Table VII). The results are also affected by the rate of addition of permanganate; gradual addition leads to an error of 4.1% but addition of 97-98% of the theoretical volume of $KMnO_4$ at the beginning leads to results with errors varying form 0.0 to 0.43%.

TABLE VII

TITRATION OF 0.1354N Cr^{+3} (AS CHROMITE DILUTED TO 50 ml) IN 0.1N NaOH WITH 0.1548N $KMnO_4$, N_2 ATMOSPHERE, Fe^{+3} IRON AND NaCl CATALYST

Rate of adding $KMnO_4$	Vol. of Cr^{+3} solution	Theor.vol. of $KMnO_4$	Max.inflec. per 0.1 ml $KMnO_4$ mv	mg Cr present	mg Cr found	Error %
1 ml $KMnO_4$ each time	4 ml	5.84 ml	240	9.39	9.005	4.1
5.4 ml $KMnO_4$	„	„ „	209	„	9.326	—0.68
8.5 ml „	6 „	8.76 „	121	14.084	14.084	nil
11.4 ml „	8 „	11.68 „	74	18.779	18.698	—0.43

SUMMARY

Determination of chromium by oxidation of chromite with permanganate does not give accurate results. $KMnO_4$ is reduced to MnO_2. Titration of $KMnO_4$ with Cr^{+3} solution in the presence of 0.8-1.5*N* NaOH and Ba^{+2} ions yields manganate and gives good results. In the absence of Ba^{+2} ions and in the presence of 0.5-2*N* NaOH reduction of $KMnO_4$ passes quantitatively to MnO_2.

Cr^{+3} can be determined by adding the chromic solution to $KMnO_4$ while stirring in presence of 1*N* NaOH and Ba ^{2} ions, or 2.5*N* NaOH in the absence of Ba^{+2} ions. The excess $KMnO_4$ is then back-titrated with formic acid.

RÉSUMÉ

Le dosage du chrome par oxydation du chromite au moyen de permanganate ne donne pas des résultats précis; $KMnO_4$ est réduit en MnO_2. La titration du permanganate par Cr^{+3} en présence de NaOH 0.8-1.5*N* et d'ions Ba^{+2} conduit au manganate et donne de bons résultats. En l'absence d'ions Ba^{+2} et en présence de NaOH 0.5 à 2*N*, $KMnO_4$ est réduit quantitativement en MnO_2. Cr^{+3} peut être dosé comme suit: on ajoute la solution à analyser à une solution étalon de $KMnO_4$, en présence de NaOH *N* et d'ions Ba^{+2}, ou en présence de NaOH 2.5*N* et en l'absence d'ions Ba^{+2}, en agitant le mélange. L'excès de $KMnO_4$ est ensuite titré par l'acide formique.

ZUSAMMENFASSUNG

Die Bestimmung des Chroms durch Oxydation von Chromit mit Permanganat gibt keine genauen Resultate. Das Permanganat wird zu MnO_2 reduziert. Die Titration von $KMnO_4$ mit Chromiionen zu Manganit in der Gegenwart von 0.8-1.5*N* NaOH liefert in Anwesenheit von Ba^{+2} Ionen gute Werte. Bei Fehlen von Ba^{+2} geht die Reduktion bis zu MnO_2 vor sich, wenn 0.5 bis 2*N* NaOH vorhanden sind, wobei gute Ergebnisse erhalten werden.

Cr^{+3}-Ionen können durch Zusatz der Chromlösung zum Permanganat unter Rühren bestimmt werden, wenn 1*N* NaOH und Ba^{+2}-Ionen oder 2.5*N* NaOH in Abwesenheit von Ba^{+2}-Ionen, vorhanden sind. Das überschüssige Permanganat wird mit Ameisensäure zurücktitriert.

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REACTIONS OF METAL IONS WITH DITHIZONE IN MOLTEN NAPHTHALENE *

by

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INTRODUCTION

A comparative study has been made of the properties of dithizone when dissolved in molten naphthalene and when used, conventionally, in a chloroform solution. This includes both the properties of the reagent and the sensitivity and selectivity of its reactions with metal ions.

The versatility of the reagent, dithizone, in the qualitative and quantitative analysis of metal ions is well known. Numerous references can be found which discuss the proposed structures of the reagent and its reaction products as well as its analytical applications[7,9,10,11,13,15,16]. Although the reagent alone is completely lacking in selectivity, careful adjustment of pH and choice of masking agents render it selective.

FEIGL AND BAUMFELD[8] have reported the use of molten 8-hydroxyquinoline in the detection of several metal ions. WEST AND GRANATELLI[14] have extended this investigation by noting, microscopically, the crystal habit of metal-8-hydroxyquinolates in a melt of the reagent. The present authors have observed the reactions of dithizone in molten naphthalene with several metal salts. The color intensity and high melting point of the reagent preclude its use without dilution. Naphthalene was chosen as solvent because it was inert and relatively low melting. Bismuth, antimony, mercury, cadmium, and tin reacted quickly with the reagent and all except mercury were found to absorb in about the same region of the visible spectrum. The reaction of bismuth with dithizone in the molten solvent system was sensitive to 0.004 micrograms of bismuth and has been reported as a spot test for that ion[2].

Absorption spectra were measured with a device designed to replace the conventional cell holder compartment of the Beckman DU Spectrophotometer, which device could be used to heat the sample above the melting point of naphthalene. Absorption spectra were obtained with this heater unit for bismuth, tin, mercury, antimony, and cadmium dithizonates and dithizone in the molten

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naphthalene. These spectra were found to correspond to those of the dithizonates in chloroform and benzene.

The rate of decomposition of the reagent was determined as first order with an activation energy of about 18 kcal/mole at 100° C.

REAGENTS

Chloroform, certified reagent, Fischer Scientific Co.

Dithizone, Matheson Co., was purified by the method proposed by the Association of Official Agricultural Chemists[1]. A stock solution of dithizone was prepared by the following procedure: Extract a chloroform solution of the reagent with $1M$ NH_4OH and after separating, acidify the basic aqueous phase with HCl. Finally, extract the acidic solution with chloroform. An aliquot of this stock solution was then diluted with chloroform to give an optical density of 0.346 at 620 mμ corresponding to a molar concentration of 10^{-5} [5].

The naphthalene solution of dithizone was prepared by dissolving 100 g of naphthalene in a minimum quantity of benzene, adding 2.0 mg of dithizone to this and finally removing the benzene by vacuum. These solutions were stored in darkness.

Stock solutions of bismuth and antimony were prepared from the respective metals. Reagent grade chloride salts of cadmium, tin(II), mercury(II), bismuth, and antimony(III) were used where the salt was added directly to the dithizone in molten naphthalene.

EXPERIMENTAL

The dithizonates of mercury(II), cadmium, bismuth, antimony(III), and tin(II) in molten naphthalene were obtained by heating the solid reagent solution to slightly above the melting point of naphthalene and adding the appropriate metal salt. The color of the dithizonate developed quickly in each case. This solution was transferred to a 10-mm quartz cell and its light absorption measured against molten naphthalene using the Beckman DU Spectrophotometer. The heating unit adapted for use with this instrument is pictured in Fig. 1. Aluminum blocks through which water is circulated make up the sides of the unit, thus protecting both the photocell compartment and the prism unit from excessive heat. Temperatures up to 150° C were obtained through 20-gauge nichrome wire wound on alundum cores as indicated in Fig. 1. Stainless steel reflectors backed the alundum cores and were in turn backed by asbestos paper. The cell holder is the standard Beckman accessory from which the two end units have been cut to allow for movement of the holder without danger of shorting the heating elements. The slide mechanism is precisely stopped to assure reproducible positioning of the cell in the light path. Copper tubes extend from the holes in the aluminum blocks to the sides of the cell holder, thus minimizing stray light.

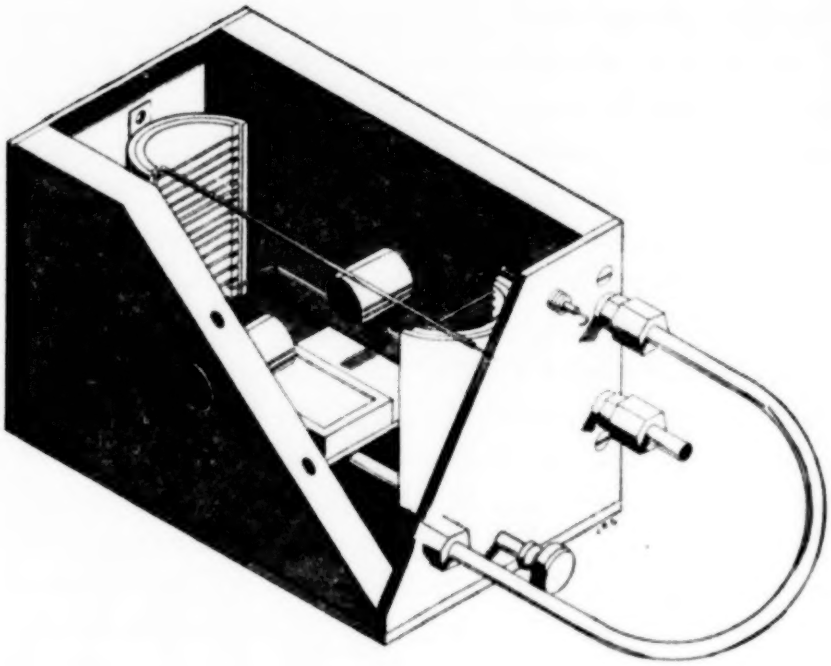


Fig. 1. Heating unit for use with Beckman DU spectrophotometer.

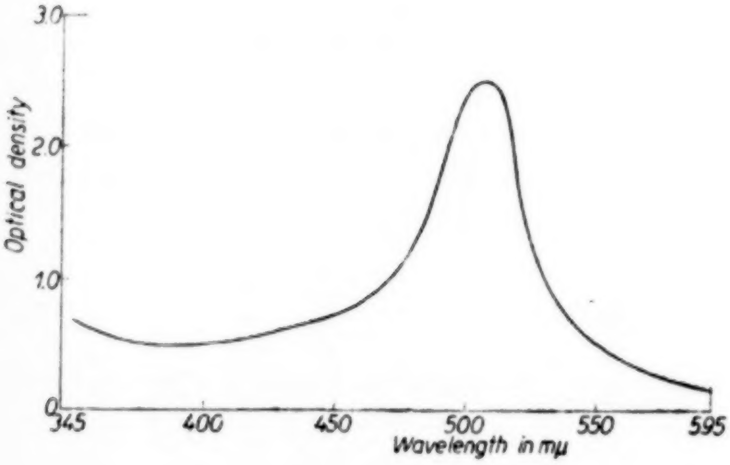


Fig. 2. Bismuth dithizonate in molten naphthalene.

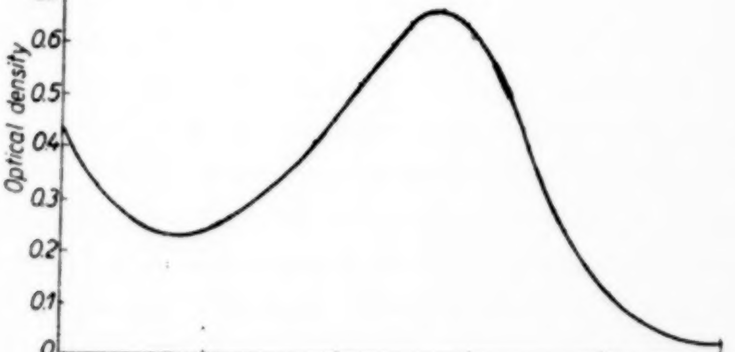


Fig. 3. Mercury dithizonate in molten naphthalene.

The interior of these tubes, as well as the aluminum inner surfaces, are painted a dull black. A chromel-alumel thermocouple was inserted through the small hole in the cover of the unit to measure the temperature of the solution in the cell. The temperature, measured with a Wheelco thermocouple potentiometer, may be controlled within $\pm 3°$ C using a Powerstat variable transformer.

Absorption spectra for mercury(II), cadmium, bismuth, antimony(III), and tin(II) dithizonates in molten naphthalene were measured with this device. These spectra are presented in Figs. 2, 3, 4, 5 and 6. The absorption spectrum of the reagent is plotted in Fig. 7. These spectra correspond reasonably well with those of the dithizonates extracted into benzene and chloroform. The absence of an appreciable maximum at 620 mμ in Fig. 7 is due to decomposition of the reagent before optical density could be measured at the longer wavelengths. The absorption spectrum of antimony(III) dithizonate has not been reported and, in fact, FEIGL[7] does not list this ion among those forming dithizonates. However, it was found that when a 1.2*N* HCl solution of antimony(III) ions was extracted with benzene-dithizone, a reddish-brown organic phase resulted. This extraction is not quantitatively applicable and the sensitivity limit of the reaction is not low enough to offer advantages over existing methods for detecting antimony. The absorption spectra of antimony dithizonate in the two media are essentially identical.

The rate of decomposition of dithizone in molten naphthalene was determined from plots of the logarithm of optical density at 630 mμ *vs.* time. At 100°, 110°, and 137° C, the rate data indicate first-order reaction with rate constants 0.07, 0.14, 0.28 min^{-1}, respectively. The activation energy at 100° C calculated from the ARRHENIUS equation is approximately 18 kcal/mole.

DISCUSSION

The structure of dithizone and its reaction products with metal ions has been the subject of much investigation. CORWIN AND JACKSON[6] confirmed the structure of the reagent postulated by FISCHER[9]. Utilizing the method of continuous variations[12], COOPER AND HIBBITS[4] have substantiated the findings of earlier workers[3,9] that the ratio of dithizone to lead in the complex is 2 : 1. COOPER AND SULLIVAN[5] have indirectly determined the mole ratio of metal ion to dithizone for zinc, mercury(II), and silver dithizonates. This was done by calculating the molecular extinction coefficient for dithizone from measurements of optical density on lead dithizonate in which the mole ratio is known to be 1 : 2. They found that the molecular extinction coefficient for dithizone calculated from optical density measurements on zinc, mercury(II), and silver dithizonates, assuming the mole ratio of metal ion to dithizone to be 1 : 2, 1 : 2 and 1 : 1, respectively, to be the same as that obtained by similar treatment of the lead dithizonate. Thus, the validity of the assumption was established.

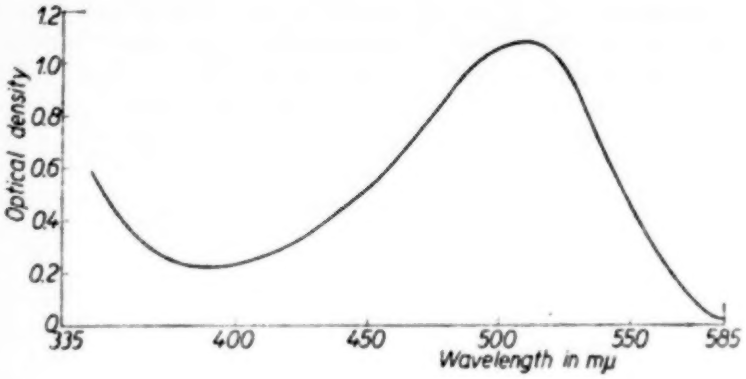


Fig. 4. Antimony dithizonate in molten naphthalene.

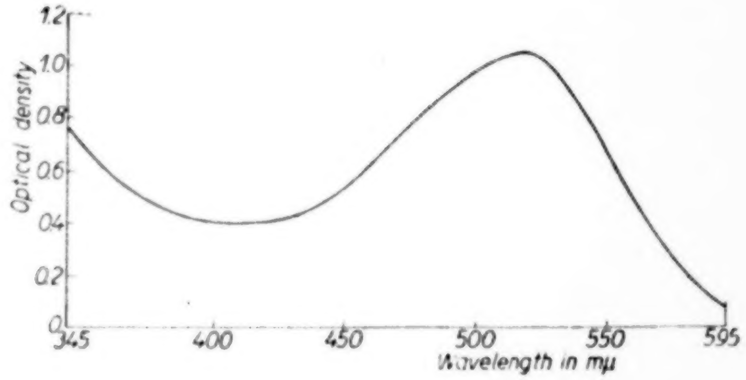


Fig. 5. Cadmium dithizonate in molten naphthalene.

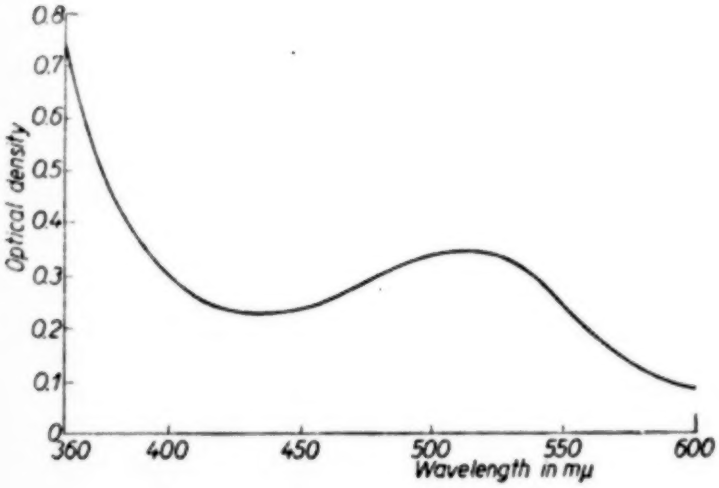


Fig. 6. Tin dithizonate in molten naphthalene.

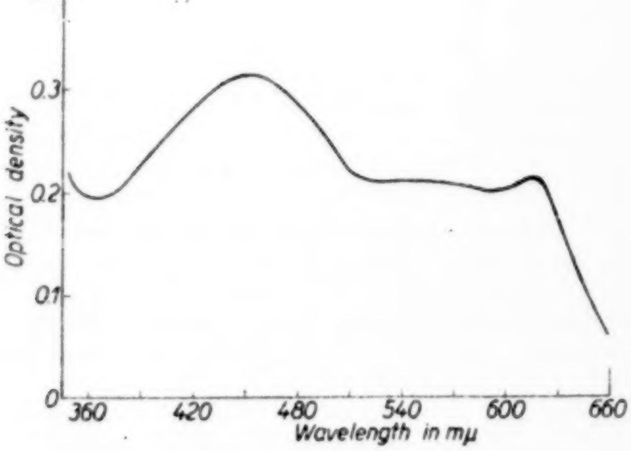
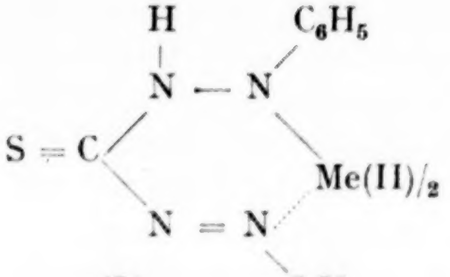


Fig. 7. Dithizone in molten naphthalene.



(I)

Because of the similarity in the absorption spectra of a metal dithizonate in the two media, benzene and molten naphtalene it is concluded that the same complex exists in both media, probably an inner complex of the type (I).

SUMMARY

A comparative study has been made of the reactions of metal ions with dithizone in the two media, chloroform and molten naphthalene. The absorption spectra of several metal dithizonates, prepared in molten naphthalene, were recorded and were found to be the same as those of the dithizonates obtained by extraction of metal ions from aqueous solution with chloroform-dithizone.

RÉSUMÉ

Une étude comparative a été effectuée sur le comportement des ions métalliques avec la dithizone dans deux milieux: chloroforme et naphtalène fondu. Les spectres d'absorption de plusieurs dithizonates métalliques, formés dans le naphtalène fondu ont été déterminés. Ils sont identiques à ceux des dithizonates obtenus par extraction des ions métalliques en solution aqueuse, au moyen d'une solution de dithizone dans le chloroforme.

ZUSAMMENFASSUNG

Es wurde eine vergleichende Untersuchung durchgeführt über das Verhalten von Metallionen mit dem Dithizon in zwei verschiedenen Milieus: Chloroform und geschmolzenes Naphtalin. Die Absorptionsspektren mehrerer Metalldithizonate, welche in geschmolzenem Naphtalin erhalten wurden, sind bestimmt worden. Sie sind denjenigen identisch, welche mittels Extraktion der Metallionen in wässeriger Lösung durch eine Chloroformlösung von Dithizon erhalten wurden.

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THE EFFECT OF ETHYLENEDIAMINETETRAACETIC ACID ON THE FERROUS/FERRIC AND CUPROUS/CUPRIC REDOX SYSTEMS

by

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It is well-known that the addition of a complexing agent to a redox system may alter the value of the oxidation potential and enhance the reducing or oxidizing power of the couple dependent on which oxidation state is the more firmly bound. Accordingly, it is not unusual to find a reversal of the normal redox reactions of the system. Examples are, the oxidation of ferrous iron by cupric copper in the presence of an appreciable excess of ammonium thiocyanate[1]

$$Cu^{+2} + Fe^{+2} + 7\,CNS^{-} = [Fe(CNS)_6]^{-3} + CuCNS$$

and the reduction of iodine solutions by ferrous salts in the presence of an equivalent amount of ethylenediaminetetraacetic acid (EDTA).

$$2Fe^{+2} + I_2 \xrightarrow{EDTA} 2Fe^{+3} + 2\,I^{-}.$$

Molybdates, selenates and silver salts are also reduced by ferrous sulphate in the presence of EDTA. PŘIBIL, SIMON AND DOLEŽAL[2] found that iodine was quantitatively reduced between pH 4-6 and that the oxidation potential of the Fe^{+2}/Fe^{+3} system was reduced from 0.771 v to 0.117 v * on addition of the complexone. Since the present study was initiated, PŘIBIL has applied this reaction to the potentiometric determination of silver[3].

The present paper describes our studies of the ferrous/ferric and cuprous/cupric ethylenediaminetetraacetate systems.

Whereas the complexes formed between EDTA and divalent cations are found to be stable in alkaline or neutral solutions, they are almost completely dissociated in acid solution with the result that at a relatively low pH most divalent cations give their normal reactions even in the presence of considerable amounts of complexone. On the other hand, the complexes with the trivalent cations are, in general, much more stable, and remain undissociated at lower pH values. The preferential complexing of the trivalent metals is probably due to a fuller utilization of the possible coordinating centres in the EDTA molecule by these cations. Divalent metals generally do not occupy all the possible positions.

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* The British system of potentials is used here, *i.e.*, the more positive the oxidation potential, the more powerful is the system as an oxidant.

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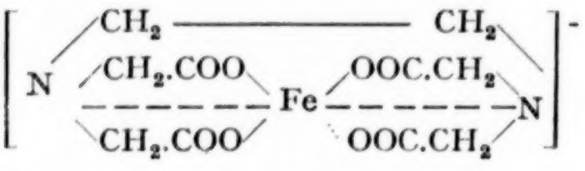
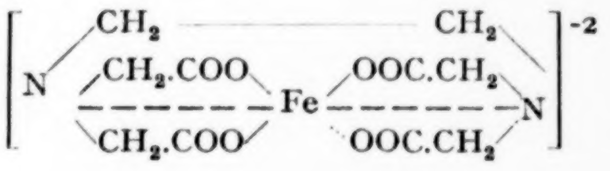


Ferric-EDTA complex



Ferrous-EDTA complex

whereas tetravalent metals form normal salts without showing much tendency to develop coordinate bonds. Accordingly, the addition of EDTA to a ferrous/ferric system results in a marked decrease in the concentration of free ferric ions with the result that ferrous ions are more easily oxidized to replace the deficiency of ferric ions. In effect, ferrous iron becomes a much more powerful reductant in the presence of EDTA.

In the cuprous/cupric system, the higher oxidation state again appears to be preferentially complexed. Cupric copper forms a very stable complex with EDTA; nickel is the only other common divalent cation which is more firmly bound. No information is available about the cuprous-EDTA complex, but since monovalent ions such as silver and thallium form only very weak complexonates, it was assumed that any stabilization of the cuprous ion by EDTA is relatively weaker than the stabilization of the cupric ion.

Thus, in the presence of EDTA, the reaction of cupric copper with iodides to yield free iodine is reversed and cuprous salts will reduce iodine to iodide

$$2Cu^+ + I_2 \xrightarrow{EDTA} 2I^- + 2Cu^{+2}.$$

Variation of oxidation potential with acidity

SCHWARZENBACH and his co-workers have shown that the instability constants of EDTA-metal complexes are markedly affected by hydrogen ion concentration. Because of the different effects of pH on the complexes of the different valency states of a metal ion, a change of pH produces a change in the oxidation potential of the redox system. We have examined the variation of the oxidation potentials of the two systems in the presence of EDTA over a range of acidity to establish a practicable pH range in which the enhancement of reducing power is a maximum.

Fig. 1 was obtained as described subsequently, with 0.1*M* ferrous sulphate solution, together with slightly more than the theoretical amount of the disodium salt of EDTA. The reducing power of the ferrous state increased steadily with increasing pH until a plateau (*ca.* 0.120 v) was reached between pH 4-6. Thereafter the oxidation potential again decreased rapidly attaining a value of —0.2 to —0.3 v at about pH 11. However, above pH 6 ferric hydroxide, or a hydrated form of the EDTA complex of ferric iron[4] precipitated from solution.

Fig. 2*A* was obtained as described subsequently with a 0.1*M* cuprous chloride solution together with slightly more than the theoretical amount of EDTA (disodium salt). The reducing power of the cuprous-EDTA solution increased steadily with increasing pH until a plateau was reached between pH 3-5. Above pH 6 the oxidation potential again decreased rapidly, but precipitation of cuprous oxide occurred. A second curve (Fig. 2B) was obtained, using ammonium hydroxide rather than sodium hydroxide to adjust the pH. This shows only a slight divergence from the former curve, the difference being due to partial complexing of the copper ions by ammonium ions. The presence of the ammonium ions, however, prevented the precipitation phenomenon above pH 6. Finally, the curve for the effect of ammonia on the oxidation potential of the cuprous/cupric system in the absence of EDTA was obtained (Fig. 2C). It may be postulated that the effect of the ammonia is somewhat additive to the cuprous/cupric-EDTA curve

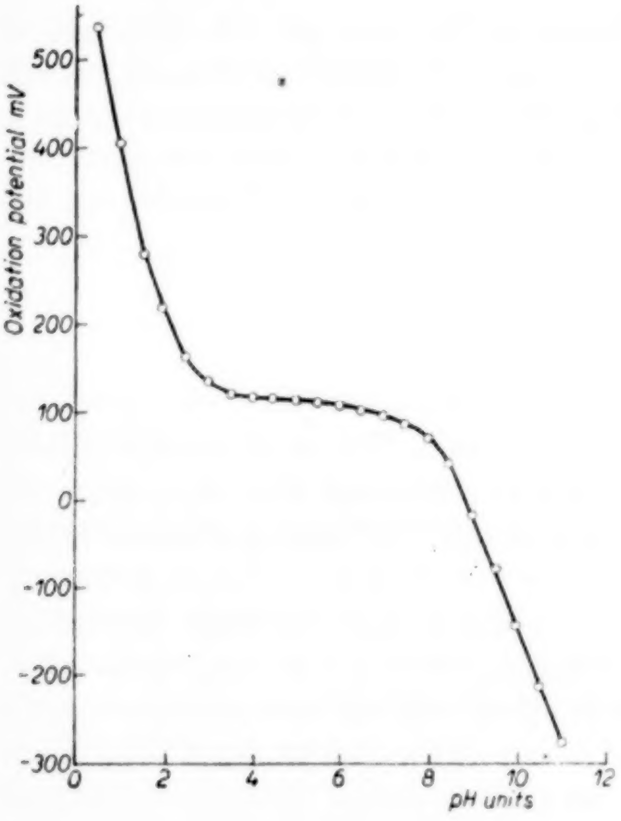


Fig. 1.

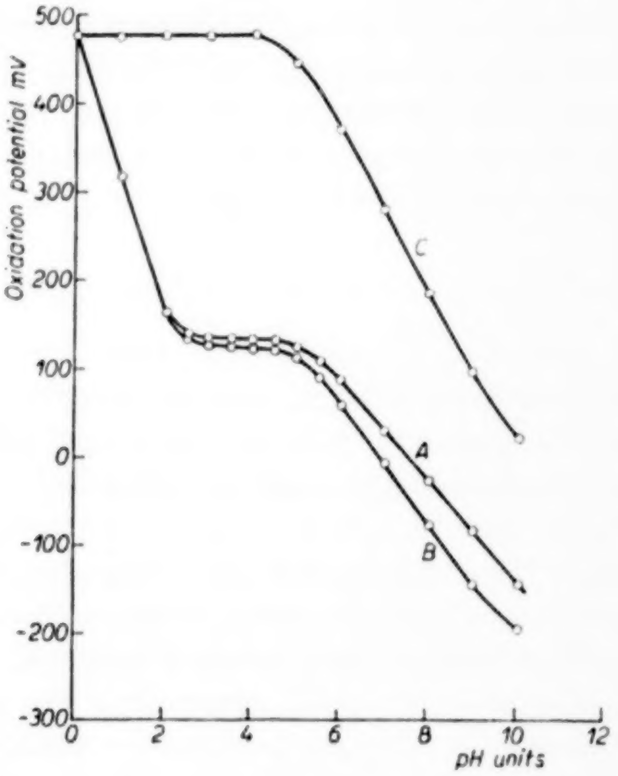


Fig. 2.

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(Fig. 2A) above pH 2, the steep gradient of the cuprous/cupric-ammonia curve being reflected in the increased gradient of Fig. 2B above pH 5.

The potentials recorded in Figs. 1, 2A and 2B for pH values below 2.5 can only be regarded as approximate, because free EDTA precipitated from solution. The values recorded were obtained by rapid measurement after adjusting the pH of the solution to the required value. All measurements were made in an atmosphere of carbon dioxide.

It may be concluded that the optimum pH values for the use of ferrous ethylenediaminetetraacetate as a reductimetric titrant lie between pH 4-6 which is in accordance with the findings of PŘIBIL, SIMON AND DOLEŽAL (*loc. cit.*) on the reduction of iodine solutions. Similarly the optimum acidity for the use of cuprous ethylenediaminetetraacetate is pH 3-5, the value of the oxidation potential at this pH being little different from the figure quoted in the literature for the free cuprous/cupric system.

Stability of ferrous ethylenediaminetetraacetate solutions

Several 0.1 *N* solutions of ferrous ethylenediaminetetraacetate were prepared from ferrous sulphate and the disodium salt of EDTA. The pH of these solutions was adjusted to different values and the solutions were then titrated, at intervals over several days, against a standard iodine solution, buffered at pH 5. The solutions were stored in ordinary glass-stoppered vessels and were not protected from the atmosphere in any other way. The solutions were increasingly susceptible to aerial oxidation as the pH value rose from 3-10. Below pH 2.5 the precipitation of free EDTA could not be prevented, even by the addition of calcium acetate.

A layer of light petroleum ether was maintained in the storage vessel containing the ferrous ethylenediaminetetraacetate, to retard aerial oxidation, and the solution was fed into a burette by a siphon tube and a two-way tap at the foot of the apparatus. A layer of petroleum ether protected the titrant in the burette. A solution stored in this way showed no measurable tendency towards oxidation over a period of three days, but thereafter it was slowly oxidized. By storing some samples in an inert atmosphere, it was shown that the deterioration was due to aerial oxidation rather than attack on the solvent or other solutes. These samples yielded unchanged titres even after several weeks.

Rather than store the titrant in an inert atmosphere, a separate solution of 0.1 *N* ferrous ammonium sulphate was used as titrant, in conjunction with a 10 % solution of EDTA (disodium salt) which was added to the solution being titrated. When the former was stored under a layer of light petroleum ether it gave an unchanged titre over a period of more than 10 days. By this separate solution technique, a substantially stable titrant was obtained without the necessity of having the cumbersome apparatus required for storing the reagents in an inert atmosphere.

Stability of cuprous ethylenediaminetetraacetate solutions

Text-books of inorganic chemistry state that cuprous chloride is appreciably soluble only in solutions of hydrochloric acid or alkali chlorides. An acid solution of cuprous chloride readily dissolved the disodium salt of EDTA in the cold, but on standing the solution deposited free EDTA. A neutral solution of cuprous chloride in ammonium chloride dissolved the disodium salt of EDTA only slowly, even on warming, and on standing, this solution became blue in colour and deposited EDTA together with a small amount of a reddish brown powder. The formation of the blue colour seemed to support the idea that the cuprous-EDTA complex could disproportionate into cupric-EDTA and copper metal as suggested by PECSOCK[5], but the reddish brown powder was shown to be cuprous oxide and not copper metal.

The cuprous oxide was formed by hydrolysis of the cuprous ions:-

$$2Cu^+ + H_2O \rightarrow Cu_2O + 2H^+$$

The EDTA acted as a buffer, removing the hydrogen ions liberated and so favouring the hydrolysis, and the free EDTA so formed was deposited. When the solution was made sufficiently acid to prevent hydrolysis, free EDTA alone was precipitated.

The fact that the cuprous-EDTA solution became blue in colour, but copper metal was not formed, was explained when it was shown that finely divided copper metal would in fact dissolve in EDTA (disodium or trisodium salts), so that although disproportionation might occur, the copper metal was complexed by EDTA before it could precipitate.

Thus, a composite cuprous-EDTA solution was not practicable. An acid solution of cuprous chloride, however, rapidly absorbed atmospheric oxygen, and even when stored under a layer of petroleum ether the solution did not maintain its titre (against potassium dichromate) over a period of 24 hours. The acidity of the solution was varied from $5N$ to $0.5N$ with respect to hydrochloric acid, but the stability was not improved, and neutral or alkaline solutions of cuprous chloride in ammonium chloride were also unstable.

A column of spongy silver was interposed between the storage vessel and the burette, in an attempt to supply the latter with a cuprous chloride solution of a constant strength with respect to cuprous ion. This was successful when the solution was $1N$ with respect to hydrochloric acid. The cuprous chloride solution, when stored in this way, was shown to be stable indefinitely by potentiometric titration against potassium dichromate. The useful life of the silver reductor was indicated by the progress of a purple-brown zone which spread slowly down the column.

Use of the ferrous and cuprous-EDTA complexonates as reductimetric reagents

Both ferrous-EDTA and cuprous-EDTA (using the separate solution technique), after standardization against iodine or dichromate, were used for the quantitative determination of several oxidizing ions such as dichromate, vanadate, trivalent manganese and also iodine. Weaker oxidants such as iodate, bromate and chlorate were determined indirectly by titrating iodine liberated from potassium iodide.

Neither titrant, however, had any advantages over existing reagents; consequently, no experimental details are given for these titrations. Ferrous-EDTA can, of course, be used for the determination of silver as described by PŘIBIL[3], but cuprous EDTA, because of its weaker reducing power, can only be used for this titration in strongly ammoniacal solution.

The reducing properties of both reagents lie intermediate between those of stannous and titanous chlorides.

THEORETICAL

SCHWARZENBACH AND HELLER[4] have given a full theoretical treatment to explain the enhancement of the reducing power of the ferrous ion in the presence of EDTA. A similar calculation for the cuprous/cupric system, assuming that there is little, if any, complexing of the cuprous ion by EDTA compared with the complexing effect of chloride ions, leads to a value of -0.621 v for the measured oxidation potential compared to the actual value of 0.132 v.

The value of this observed potential is little different from that of the simple cuprous/cupric couple (0.153 v[6]) thus implying that in the presence of EDTA both the cuprous and cupric states must be complexed to almost the same extent. Now the formation constant of the cupric-EDTA complex[7] is $10^{18.38}$ and that of the cuprous-chloride complex[6], is only 10^6, which is very small by comparison and may be neglected. Thus, the formation constant of the cuprous-EDTA complex may also be of the order of 10^{18}.

Thus we have the unusual situation in which a complex appearing to have a high formation constant is unstable. Further work is necessary to establish the existence and properties of such a complex.

EXPERIMENTAL

Measurement of oxidation potentials

Solutions required:

0.1*N* ferrous sulphate

0.1*N* cuprous chloride (prepared by reducing an acid 0.1*M* solution

of AnalaR cupric chloride in a silver reductor).
10% EDTA (disodium salt)
0.1N potassium dichromate
5N sulphuric acid
5N hydrochloric acid
5N ammonia solution

20 ml of the appropriate solution were acidified and were titrated potentiometrically with 0.1N dichromate. A further 20 ml of the original solution were then added in excess, followed by 20 ml of the EDTA solution.

The pH of the solution was adjusted to the required value and the potential was measured as rapidly as possible, using a direct reading mains pH meter/potentiometer. The values found for the oxidation potentials were then converted to the hydrogen scale.

The above measurements were made with the solutions protected from aerial oxidation by an atmosphere of carbon dioxide gas.

ACKNOWLEDGEMENTS

During the course of this work, Professor R. PŘIBIL (Charles University, Prague) reported on the use of a ferrous EDTA solution for the potentiometric determination of silver salts. We wish to thank Professor PŘIBIL for his generosity in consenting to our continuing these studies in work he has pioneered.

Two of us, D.G. and T.S.W., are indebted to the Department of Scientific and Industrial Research for grants enabling this work to be undertaken.

SUMMARY

The effect of ethylenediaminetetraacetic acid on the redox systems Fe^{+2}/Fe^{+3} and Cu^{+}/Cu^{+2} has been examined. In each case the oxidation potential of the system was markedly reduced, thus making the lower valency state a more powerful reductant. It has been established that the oxidation potentials of the two systems, in the presence of EDTA, at pH 4-5, are 0.12 and 0.13 v respectively.

Because of these enhanced reducing powers, attempts were made to use ferrous-EDTA and cuprous-EDTA as reductimetric reagents. A variety of oxidants was in fact successfully titrated, but neither titrant possessed any advantage over existing reagents.

The reducing properties of both systems lie intermediate between those of stannous and titanous chlorides.

Theoretical considerations suggest the existence of a cuprous-EDTA complex with a formation constant of *ca.* 10^{18}.

RÉSUMÉ

L'influence de l'acide éthylènediaminotétraacétique sur les systèmes rédox Fe^{+2}/Fe^{+3} et Cu^{+}/Cu^{+2} a été examinée. Dans chacun des cas le potentiel d'oxydation du système est considérablement abaissé, augmentant ainsi le pouvoir réducteur de l'ion à sa valence inférieure. Les potentiels d'oxydation de ces deux systèmes, en présence d'EDTA, à un pH 4-5 sont respectivement 0.12 et 0.13 v.

References p. 114.

En raison de ce pouvoir réducteur, des essais ont été faits avec Fe^{+2}-EDTA et Cu^{+}-EDTA. En effet un grand nombre d'oxydants ont pu être ainsi titrés avec succès, mais ni l'un ni l'autre de ces réducteurs ne présentent des avantages sur les réactifs existants. Les propriétés réductrices de ces deux systèmes se placent entre celles des chlorures stanneux et titaneux. Des considérations théoriques font supposer l'existence d'un complexe Cu^{+}-EDTA avec une constante de formation d'environ 10^{18}.

ZUSAMMENFASSUNG

Der Einfluss der Ethylendiaminotetraessigsäure auf die Redoxsysteme Fe^{+2}/Fe^{+3} und Cu^{+}/Cu^{+2} ist untersucht worden. In beiden Fällen ist das Oxydationspotential des Systems beträchtlich erniedrigt, und erhöht somit das Reduktionsvermögen des Ions zu seiner niedrigen Wertigkeit. Die Oxydations-potentiale dieser beiden Systeme bei einem pH von 4-5 in Gegenwart von EDTA sind bezw. 0.12 und 0.13 V. Auf Grund dieses Reduktionsvermögens sind Versuche mit Fe^{+2}-EDTA und mit Cu^{+}-EDTA gemacht worden. In der Tat konnte auf diese Weise eine grosse Anzahl von Oxydationsmitteln mit Erfolg titriert werden, aber weder das eine noch das andere Reduktionsmittel bietet gegenüber den bereits existierenden einen Vorteil. Die reduzierenden Eigenschaften von diesen beiden Systemen liegen zwischen denen des Zinn- und des Titanchlorids. Theoretische Betrachtungen führen zur Annahme, dass sich ein Cu^{+}-EDTA-Komplex bildet mit einer Bildungskonstanten von ungefähr 10^{18}.

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TITRATIONS WITH EXTRACTIVE END-POINTS
I. THE PERMANGANATE TITRATION

by

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INTRODUCTION

The triphenylmethylarsonium cation has been shown to form analytically useful salts, soluble in organic solvents with anionic complexes of iron[1], antimony[2], cobalt[3] and copper[4], and in this paper its use in the extraction of the permanganate ion at the end-point of permanganate titrations is examined.

Potassium permanganate has long been recognised as a convenient reagent for the titration of certain oxidizable substances, notably iron(II), arsenite and oxalate, since it acts as its own internal indicator. However, its use has been severely limited by the masking of the end-point by appreciable quantities of coloured cations, necessitating the separation of the element to be estimated before the titration could be performed. Attempts to overcome this disadvantage have included those of LURÉ AND TAL[5], who plotted the increase in permanganate concentration after the end-point by means of a photo-electric colorimeter and extrapolated back to the end-point, and of GOTO[6], who obtained a more intense colour change at the end-point, by the use of fluorescent indicators. The first of these methods is clearly a tedious one, and both would be limited in the amounts of coloured ions which could be tolerated.

The only previous titration involving an extractive end-point appears to be that of thiosulphate or arsenite with standard iodine solution, excess of which was extracted with carbon tetrachloride[7].

DISCUSSION

In the present work, a stable, deep purple crystalline compound, triphenylmethylarsonium permanganate, $(Ph_3MeAs)(MnO_4).\frac{1}{2}H_2O$, has been isolated. The compound, which was prepared by the addition of triphenylmethylarsonium chloride solution to potassium permanganate solution, was readily extracted by chloroform, ethylene dichloride or tetrachloroethane to form a deep purple solution which could be decolourised by shaking with an aqueous solution of a suitable reducing agent.

The method of use in permanganate titrations consisted essentially of the addition of a small amount (0.5 to 2 ml) of 5% $Ph_3MeAsCl$ solution and 5 ml of a suitable immiscible solvent to the solution to be titrated, and then titrating with standard potassium permanganate in the usual way, shaking after each addition of $KMnO_4$ solution as the end-point was approached. The end-point was indicated by the colourless solvent layer turning pink, due to extracted $(Ph_3MeAs)(MnO_4)$, the visibility of the colour change being quite independent of the intensity of colour of the aqueous layer due to unreactive metal ions.

It is clear that the distribution coefficient of the permanganate salt with the large cation must be sufficiently high to give a small titration error, but not high enough to prevent rapid exchange of the permanganate with the water layer, otherwise a false end-point would be obtained. Results obtained showed that the suggested compound met these requirements. Tetraphenylarsonium permanganate has been previously prepared[8] but its formation was not suggested in the present regard, due, no doubt, to its solvent water distribution coefficient being too high.

The method has been successfully applied to the titration of iron(II) (Tables I and II), arsenite (Table III) and oxalate (Table IV) with solutions of potassium permanaganate ranging from *N*/10 to *N*/100, in the presence of molar ratios of cobalt(II), nickel(II), copper(II), chromium(III) and manganese(II) ions up to 100 or even 200 times that of the reducing agent. It is thus clear that this modification greatly simplifies the estimation of iron in its alloys, rendering its separation unnecessary in many cases.

The back titration of permanganate with iron(II), arsenite and oxalate was equally satisfactory, and was applied to STAMM's method[9] of estimating organic and inorganic compounds with alkaline potassium permanganate. However, the back titration was only possible in acid solution, as alkaline solutions emulsified the organic layer. The results obtained using the modified STAMM's method are summarised in Table V.

The blanks were found to be conveniently low, being approximately 0.03 ml for *N*/10 $KMnO_4$, (including back titration), 0.07 ml for *N*/50, and 0.11 for *N*/100.

The results by the extractive method were compared with those obtained by potentiometric and the normal visual titrations. Results in Tables I to IV (all corrected for blanks), demonstrate that the values obtained by the extractive method were not appreciably different from those by the potentiometric titration, while with the normal visual method, the end-point could not be seen in many cases, and in others, an appreciably high reading was obtained.

Large concentrations of sulphate, nitrate and phosphate ions were without effect, as were moderate amounts of chloride ion. As would be expected, large concentrations of chloride ion gave a high titration figure, but this could be overcome by the addition of a large concentration of Mn(II) ion to reduce the redox potential of the MnO_4^-/Mn^{+2} couple, together with phosphate to lower the Fe^{+2}/Fe^{+3} redox potential.

The volume of 5% $Ph_3MeAsCl$ solution used was not critical, appreciably smaller and larger volumes than those suggested being equally suitable, however, large amounts (*i.e.* 10 ml or more) increased the blank slightly, due probably to the chloride ion, as $Ph_3MeAsNO_3$[10] did not do this.

TABLE I

N/50 Fe(II) (25 ml) with *N*/50 $KMnO_4$.
Solution approximately *N* with respect to H_2SO_4.

Interfering ion	Molar ratio Ion: Fe(II)	Mean titration (ml)		
		Potentiometric	Extractive	Visual
Cu^{+2}	1 : 1	24.84	24.83	24.86
Cu^{+2}	10 : 1	24.82	24.83	24.90
Cu^{+2}	100 : 1	24.85	24.84	*
Cr^{+3}	1 : 1	24.85	24.86	24.89
Cr^{+3}	10 : 1	24.83	24.83	*
Cr^{+3}	100 : 1	24.87	24.88	*
Ni^{+2}	1 : 1	24.80	24.81	24.82
Ni^{+2}	10 : 1	24.81	24.82	24.87
Ni^{+2}	100 : 1	24.83	24.83	*
Co^{+2}	1 : 1	24.80	24.81	24.84
Co^{+2}	10 : 1	24.82	24.83	*
Co^{+2}	100 : 1	24.84	24.83	*
Mn^{+2}	1 : 1	24.85	24.86	24.87
Mn^{+2}	10 : 1	24.88	24.88	24.90
Mn^{+2}	100 : 1	24.87	24.86	24.88
PO_4^{-3}	1 : 1	24.85	24.87	24.87
PO_4^{-3}	10 : 1	24.86	24.86	24.89
PO_4^{-3}	100 : 1 (as Na_2HPO_4)	24.86	24.88	24.90
NO_3^-	1 : 1	24.83	24.84	24.86
NO_3^-	10 : 1	24.83	24.83	24.85
NO_3^-	100 : 1	24.84	24.84	24.86
Cl^-	Nil	24.85	24.86	24.87
Cl^-	1 : 1	**	24.86	24.87
Cl^-	10 : 1	**	25.03	25.04
Cl^-	100 : 1	**	25.26	25.25

* End-point could not be seen.
** Not determined.

Suitable solvents for the extraction include ethylene dichloride, tetrachlorethane and chloroform, the first being preferred on the grounds of stability and cheapness. It was necessary to purify the solvents by shaking with acid permanganate solution, then concentrated sulphuric acid, and finally fractionally distilling, in order to remove oxidizable impurities.

Similar extractive titration methods with dichromate and iodine are being studied, and will be reported subsequently.

TABLE II

N/10, *N*/50 and *N*/100 Fe(II) (25 ml) with *N*/10, *N*/50 and *N*/100 $KMnO_4$

Interfering ion	Molar ratio Ion: Fe(II)	Concentration of $KMnO_4$	Mean titration (ml)		
			Potentiometric	Extractive	Visual
Cu^{+2}	50 : 1	*N*/10	24.86	24.85	*
Cu^{+2}	100 : 1	*N*/50	24.85	24.84	*
Cu^{+2}	200 : 1	*N*/100	24.98	24.99	*
Cr^{+3}	50 : 1	*N*/10	24.94	24.93	*
Cr^{+3}	100 : 1	*N*/50	24.87	24.88	*
Cr^{+3}	200 : 1	*N*/100	24.98	24.99	*
Ni^{+2}	50 : 1	*N*/10	24.89	24.89	*
Ni^{+2}	100 : 1	*N*/50	24.83	24.83	*
Ni^{+2}	200 : 1	*N*/100	24.99	24.99	*
Co^{+2}	50 : 1	*N*/10	25.03	25.03	*
Co^{+2}	100 : 1	*N*/50	24.84	24.83	*
Co^{+2}	200 : 1	*N*/100	24.98	24.98	*
Mn^{+2}	50 : 1	*N*/10	24.98	24.99	24.98
Mn^{+2}	100 : 1	*N*/50	24.87	24.86	24.88
Mn^{+2}	200 : 1	*N*/100	24.98	24.98	25.01
NO_3^-	50 : 1	*N*/10	25.02	25.03	25.03
NO_3^-	100 : 1	*N*/50	24.84	24.84	24.86
NO_3^-	200 : 1	*N*/100	24.97	24.98	25.00
PO_4^{-3}	50 : 1	*N*/10	25.05	25.05	25.05
PO_4^{-3}	100 : 1	*N*/50	24.86	24.88	24.90
PO_4^{-3} (as Na_2HPO_4)	200 : 1	*N*/100	24.99	24.99	25.02
PO_4^{-3}	50 : 1	*N*/10	25.03	**	25.05
PO_4^{-3}	100 : 1	*N*/50	24.87	**	24.88
PO_4^{-3} (as H_3PO_4)	200 : 1	*N*/100	24.98	**	24.99

* End-point could not be seen.

** The permanganate colour was visible in the aqueous layer but did not extract into the ethylene dichloride until approximately 0.4 ml excess $KMnO_4$ had been added. Hence acid concentration should not exceed *N* if large quantities of phosphate are present.

Experimental

Triphenylmethylarsonium permanganate (I), $Ph_3MeAsMnO_4.\frac{1}{2}H_2O$. Excess $Ph_3MeAsCl$ (140 ml of 5% aqueous solution) was added to a saturated $KMnO_4$ solution (34 ml = 2.4 g). (The $KMnO_4$ solution was freed of impurities, according to VOGEL[11].) A deep purple solid separated, was collected by filtration and washed with water, then light petroleum (b.p. 60-90°). Yield: 85-90% (almost quantitative if extracted from reaction mixture with pure chloroform).

(I) was recrystallized by dissolving in pure dry chloroform and adding pure dry cold light petroleum (b.p. 60-90°); it appeared as an oil which readily crystallized as small shiny plates.

It was stable at room temperature, and was readily soluble in chloroform, ethylene dichloride, tetrachloroethane and acetone, slightly soluble in water and quite insoluble in light petroleum (b.p. 60-90°), ether and carbon tetrachloride. It decomposed when warmed with unsaturated solvents (e.g. $CHCl = CCl_2$) and the lower saturated aliphatic alcohols. Attempts to dry at elevated temperatures caused decomposition, so it was dried at room temperature over P_2O_5 under vacuum (0.5 mm) for 6 hours.

Calculated for $Ph_3MeAsMnO_4.\frac{1}{2}H_2O$.; C = 50.80%; H = 4.26%; As = 16.68%; Mn = 12.23%; MnO_4^- = 26.48%;

Found: C = 50.76, 50.82%; H = 4.24%, 4.24%; As = 16.80, 16.75%; Mn = 12.25; 12.28%; MnO_4^- = 26.24%, 26.28%.

MnO_4^- was estimated by adding a known excess volume of $N/10$ ferrous sulphate and back titrating with standard $N/10$ $KMnO_4$, using the extractive technique.

Procedure

The general procedure is essentially standard. The solution to be titrated is pipetted into a glass-stoppered 500 ml conical flask, fitted with a horizontal side arm, one inch long by ½ inch wide joined to the flask near the base. The correct amount of sulphuric or hydrochloric acids *etc.* (see specialized procedures) is added, together with the required volume of 5% aqueous $Ph_3MeAsCl$ solution and 5 ml of the organic solvent (ethylene dichloride or chloroform). The aqueous layer was made up to about 150 ml in all cases.

It is convenient to do a rapid titration to determine the approximate equivalence first. In the subsequent titrations the permanganate is added dropwise near the end-point, the flask being stoppered and shaken after adding each drop. The appearance of a red-purple colour in the organic layer (viewed in the side arm against a white background) indicates the end-point.

In the case of back titrations of $KMnO_4$, the procedure is identical, except that the disappearance of the colour in the organic solvent layer indicates the end-point.

TABLE III

N/10, *N*/50 and *N*/100 Arsenite (25 ml) with *N*/10, *N*/50 and *N*/100 $KMnO_4$

Interfering ion	Molar ratio Ion: Arsenite	concentration of $KMnO_4$	Mean titration (ml) Potentiometric	Extractive	Visual
Cu^{+2}	100 : 1	*N*/10	24.83	24.83	*
Cu^{+2}	200 : 1	*N*/50	25.08	25.09	*
Cu^{+2}	400 : 1	*N*/100	25.16	25.18	*
Cr^{+3}	100 : 1	*N*/10	24.82	24.82	*
Cr^{+3}	200 : 1	*N*/50	25.08	25.09	*
Cr^{+3}	400 : 1	*N*/100	25.16	25.18	*
Ni^{+2}	100 : 1	*N*/10	24.84	24.85	*
Ni^{+2}	200 : 1	*N*/50	25.06	25.06	*
Ni^{+2}	400 : 1	*N*/100	25.15	25.16	*
Co^{+2}	100 : 1	*N*/10	24.81	24.81	*
Co^{+2}	200 : 1	*N*/50	25.08	25.07	*
Co^{+2}	400 : 1	*N*/100	25.14	25.16	*
Mn^{+2}	100 : 1	*N*/10	24.84	24.83	24.84
Mn^{+2}	200 : 1	*N*/50	25.06	25.08	25.09
Mn^{+2}	400 : 1	*N*/100	25.16	25.16	25.18

* End-point could not be seen.

TABLE IV

N/10, *N*/50 and *N*/100 oxalate (25 ml) with *N*/10, *N*/50 and *N*/100 $KMnO_4$

Interfering ion	Molar ratio Ion: Oxalate	concentration of $KMnO_4$	Mean titration Potentiometric	Extractive	Visual
Cu^{+2}	100 : 1	*N*/10	24.84	24.85	*
Cu^{+2}	200 : 1	*N*/50	25.11	25.12	*
Cu^{+2}	400 : 1	*N*/100	25.21	25.21	*
Cr^{+3}	100 : 1	*N*/10	24.81	24.81	*
Cr^{+3}	200 : 1	*N*/50	25.10	25.10	*
Cr^{+3}	400 : 1	*N*/100	25.20	25.18	*
Ni^{+2}	100 : 1	*N*/10	24.86	24.86	*
Ni^{+2}	200 : 1	*N*/50	25.12	25.13	*
Ni^{+2}	400 : 1	*N*/100	25.23	25.23	*
Co^{+2}	100 : 1	*N*/10	24.86	24.85	*
Co^{+2}	200 : 1	*N*/50	25.11	25.11	*
Co^{+2}	400 : 1	*N*/100	25.24	25.24	*
Mn^{+2}	100 : 1	*N*/10	24.85	24.86	24.86
Mn^{+2}	200 : 1	*N*/50	25.13	25.14	25.16
Mn^{+2}	400 : 1	*N*/100	25.22	25.23	25.26

* End-point could not be seen.

References p. 123.

RESULTS

Tables I-V show the effect of coloured metal ions (as sulphates) on the extractive end-point, as compared with results obtained with the ordinary visual and the potentiometric methods under the same conditions. Table I shows the complete results for the titration of Fe(II) with $N/50$ $KMnO_4$, Tables II, III and IV for the sake of brevity, show results for only the highest concentration of coloured cations.

All titrations are corrected for the blank, and are the mean of three titrations. In all cases 5 ml of solvent was used; the solvent was chloroform for titration of Fe(II) with $N/10$ $KMnO_4$, and ethylene dichloride in all other cases. The reagent consisted of a 5% aqueous solution of $Ph_3MeAsCl$. All ratios of reducing agent to interfering ions were molar. 25 ml aliquots of the reducing agent were used in all titrations. $KMnO_4$ solutions ($N/10$, $N/50$ and $N/100$) were prepared according to VOGEL[11].

Fe(II) as $(NH_4)_2SO_4.FeSO_4$

Standard $(NH_4)_2SO_4.FeSO_4$ ($N/10$, $N/50$ and $N/100$) was prepared according to VOGEL[12], except that the $N/50$ and $N/100$ solutions were N with respect to H_2SO_4.

Volume of 5% $Ph_3MeAsCl$ used: 2 ml for $N/10$ $KMnO_4$, 1 ml for $N/50$, and 0.5 ml for $N/100$.

Volume of standard $(NH_4)_2SO_4.FeSO_4$: 25 ml.

Sodium arsenite

Standard solutions of sodium arsenite ($N/10$, $N/50$ and $N/100$) were prepared according to VOGEL[13]. In all cases, 25 ml aliquots of arsenite solution were taken and placed in titrating flask, together with required volume of concentrated solution of sulphate of interfering cation, water (100 ml), HCl ($10N$) (10 ml), one drop of $0.0025M$ KI solution (catalyst)[13], $Ph_3MeAsCl$ solution, and 5 ml of ethylene dichloride. The potassium iodide had to be free from iodine, as this would have extracted as brown Ph_3MeAsI_3.

Volume of 5% $Ph_3MeAsCl$ solution used: 2 ml for $N/10$ $KMnO_4$, 1 ml for $N/50$ and 0.5 ml for $N/100$.

Oxalate

Sodium oxalate (standard $N/10$, $N/50$ and $N/100$) solutions were prepared, and titrations done, according to VOGEL[14], with the addition of the required volume of $Ph_3MeAsCl$ solution (conveniently added just before heating the solution) and 5 ml of ethylene dichloride. The titrations were carried out in approximately $2N$ H_2SO_4 for $N/10$, and N H_2SO_4 for $N/50$ and $N/100$ solutions.

Volume of 5% $Ph_3MeAsCl$ used: 2 ml for $N/10$ $KMnO_4$, 1 ml for $N/50$ and 0.5 ml for $N/100$.

Total volume of aqueous layer (including solution of sulphate of coloured cation) was approximately 150 ml.

Quantitative oxidation with alkaline $KMnO_4$, using Stamm's method[9]

In all cases, excess $KMnO_4$ was back-titrated with standard *N*/10 oxalic acid in acid solution.

Volume of 5% $Ph_3MeAsCl$: 2 ml.

Solvent: Ethylene dichloride (5 ml).

TABLE V

Compound oxidized (1g molecule)	Mean equivalents of oxygen consumed	Theoretical equivalents of oxygen	Oxidation products
Phosphite	2.01	2.00	Phosphate
Iodide	8.03	8.00	Periodate
Chloride	0	0	—
Bromide	0	0	—
Iodate	2.00	2.00	Periodate
Formate	2.00	2.00	CO_2 and water
Glycerol	14.09	14.00	CO_2 and water

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SUMMARY

A method for titrations with $KMnO_4$ in coloured solutions is recommended, in which the permanganate ion is extracted as $Ph_3MeAsMnO_4$ at the end-point. The procedure is satisfactory for titrations with *N*/10, *N*/50 and *N*/100 $KMnO_4$, and for the back-titration of $KMnO_4$, in the presence of coloured ions of molar concentrations up to 400 times that of the substance titrated. A stable permanganate, $Ph_3MeAsMnO_4 \cdot \frac{1}{2}H_2O$, has been isolated.

RÉSUMÉ

Une méthode est proposée pour des titrations au permanganate dans des solutions colorées. Au point d'équivalence, l'ion permanganique est extrait sous forme de $Ph_3MeAsMnO_4$. Ce procédé est satisfaisant pour les titrations au moyen de $KMnO_4$ *N*/10, *N*/50 et *N*/100, et pour les titrations indirectes, en présence d'ions colorés, en concentration molaire 400 fois celle de la substance dosée. Un permanganate stable, répondant à la formule $Ph_3MeAsMnO_4 \cdot \frac{1}{2}H_2O$, a été isolé.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen zur Titration mit Permanganat in gefärbten Lösungen. Beim Äquivalenzpunkt wird das Permanganation in der Form von

$Ph_3MeAsMnO_4$ ausgezogen. Dieses Verfahren ist befriedigend für die Titrationen mit $KMnO_4$ $N/10$, $N/50$ und $N/100$ und für indirekte Titrationen in Gegenwart von gefärbten Ionen in molarer Konzentration, die 400 mal so gross ist wie diejenige der zu dosierenden Substanz. Ein stabiles Permanganat, welches der Formel $Ph_3MeAsMnO_4 \cdot \frac{1}{2}H_2O$ entspricht, wurde isoliert.

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DETERMINATION OF IRON IN THE PRESENCE OF LARGE AMOUNTS OF PHOSPHATE BY TITRATION WITH DISODIUM DIHYDROGEN ETHYLENEDIAMINETETRA-ACETATE

by

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CHENG, BRAY AND KURTZ* determined ferric iron in soils by direct titration with the disodium salt of ethylenediaminetetraacetic acid (Complexone III, Versenate, subsequently referred to as EDTA) at pH 2—3 using Tiron (disodium-1:2-dihydroxybenzene-3:5-disulphonate) or salicylic acid as indicator and claimed that 0.1 g $Na_2HPO_4.12H_2O$ did not interfere in the direct titration of 3—20 mg iron; they found, however, that if the soil contained an abnormally large amount of phosphate, interference with the end-point was encountered, although good results were obtained by adding excess of EDTA and back titrating with ferric solution.

Titrations of iron using excess EDTA as recommended by CHENG, BRAY AND KURTZ were found to be unsatisfactory in the presence of 0.6 g $Na_2HPO_4.12H_2O$; with salicylic acid as indicator no distinct end-point was observed and with Tiron as indicator the colour change at the end-point was poor and the recovery of iron low. It has been found, however, that 30 mg of iron can be determined in the presence of as much as 1 g $Na_2HPO_4.12H_2O$ by titrating with EDTA, using ammonium thiocyanate as indicator and extracting the red ferric thiocyanate into amyl alcohol or ether, provided the pH is 2.0—2.4 when the end-point is reached. If the pH is too low excess EDTA must be added before all the iron is complexed and no satisfactory end-point is obtained, whilst if the pH is too high the red ferric thiocyanate is not produced because ferric phosphate is formed preferentially.

The recommended procedure is to titrate rapidly with EDTA until the red ferric thiocyanate colour is discharged and then to adjust the pH to 2.3 and to back titrate with standard ferric alum solution. Alternatively, the pH can be adjusted to 2.4 before starting the EDTA titration, which is then carried out carefully until the red colour just disappears: if the latter procedure is adopted some ferric phosphate may be out of solution at the beginning of the titration

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* K. L. CHENG, R. H. BRAY AND T. KURTZ, *Anal. Chem.*, 25 (1953) 347.

(pH 2.4) but this does not matter as it gradually passes into solution as the titration proceeds.

Ferrous iron, if present, is slowly oxidized as the titration proceeds and, therefore, the total ferrous plus ferric iron is ultimately determined but in this case the forward titration with EDTA is slow. Hence if ferrous iron is present it is advantageous to oxidize it by the addition of ammonium persulphate before starting the titration (*cf.* ref. 1).

The method has been applied to hydrochloric acid extracts of deposits from steam boilers, which contained phosphate, Ca, Mg and Fe and the results were in good agreement with those obtained for iron by titanous chloride titration (after preliminary oxidation to convert all the iron to the ferric state).

TABLE I

COMPARATIVE DETERMINATION OF IRON BY TITANOUS CHLORIDE TITRATION AND BY EDTA TITRATION IN EXTRACTS FROM BOILER DEPOSITS

Sample	% Fe titanous chloride titration	% Fe EDTA titration
A	13.4	13.4
B	31.3	31.6
C	6.1	6.0

Reagents

EDTA 0.05*M*.

Dissolve 18.6 g disodium salt of ethylenediaminetetraacetic acid in distilled water and dilute to 1,000 ml.

The solution is conveniently standardized by titration against standard zinc solution (0.05*M*), prepared from pure electrolytic zinc foil, using an ammonia/ammonium chloride buffer and as indicator Solochrome Black WDFA (I.C.I.Ltd.) (Eriochrome black).

Iron alum, 0.05*M*.

Dissolve 2.4 g iron alum ($FeNH_4(SO_4)_2.12H_2O$) in distilled water and dilute to 100 ml.

Ammonium hydroxide 3*M*.

Ammonium thiocyanate 20%.

Procedure

Take an aliquot of a dilute HCl solution of the sample containing 3—30 mg iron, dilute to 25 ml, if necessary, add 0.2 g ammonium persulphate and stir to dissolve. Add $3M$ NH_4OH dropwise, with stirring, until a faint permanent turbidity forms. Transfer the solution to a 100 ml cylindrical separating funnel, add 1 ml 20% ammonium thiocyanate and 20 ml amyl alcohol. Titrate with $0.05M$ EDTA, adding 1.0 ml at a time at first and then 0.5 ml at a time. Shake well after each addition, and continue the titration until the amyl alcohol layer which separates is colourless. Run off the aqueous layer and adjust its pH to 2.3 by the addition of $3M$ NH_4OH, using a glass electrode.

Return the aqueous solution to the separating funnel and titrate with $0.05M$ iron alum, shaking well after each addition, until the amyl alcohol is faintly pink. (ml $0.05M$ EDTA — ml $0.05M$ iron alum) × 2.8 = mg iron in aliquot taken.

SUMMARY

Ferric iron, even in the presence of comparatively large amounts of phosphate, can be determined by titrating with the disodium salt of ethylenediaminetetraacetic acid (Versenate, Complexone III), using ammonium thiocyanate as indicator and extracting the red ferric thiocyanate into amyl alcohol, provided the pH is controlled at 2.0 — 2.4 at the end-point. The method has been successfully used for the determination of iron in phosphate-containing deposits from steam boilers.

RÉSUMÉ

Le fer(III), même en présence de quantités relativement grandes de phosphates, peut être dosé par titration au moyen du sel disodique de l'acide éthylènediaminotétraacétique (versenate, complexon III); on utilise alors le thiocyanate d'ammonium comme indicateur, en contrôlant le pH (2.0 à 2.4) au point final. Cette méthode a été appliquée avec succès au dosage du fer dans des dépôts de bouilleurs renfermant du phosphate.

ZUSAMMENFASSUNG

Das Eisen(III) kann, selbst bei Anwesenheit von relativ grossen Quantitäten von Phosphaten bestimmt werden durch Titration mit dem Dinatriumsalz der Ethylendiaminotetraessigsäure (Versenat, Komplexon III). Man wendet in diesem Falle das Ammoniumrhodanid als Indikator an und kontrolliert das pH (2.0 bis 2.4) beim Endpunkt. Diese Methode wurde mit Erfolg angewendet in den Kesselsteinen, welche Phosphat enthalten.

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THE DETERMINATION OF ALUMINA IN SILICATES (ROCKS AND REFRACTORIES)

by

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INTRODUCTION

Until fairly recent times the procedures for the determination of the alumina contents of silicate materials have been unsatisfactory and time consuming. The position in 1951 was summarized in a publication[1] dealing with a co-operative investigation on silicate rock analysis by analysts of international repute. The general technique for the alumina determination consisted of separating the Group III metals with ammonium hydroxide and igniting the precipitate to give the mixed oxides, R_2O_3. The alumina content was then calculated by difference from the total weight of mixed oxides after the separate determination of all other constituents (e.g. Fe_2O_3, TiO_2, P_2O_5). Various slight modifications to this technique were favoured by some analysts. One typical modification consisted of the separation of the iron and titanium from the other constituents of an acid solution of the mixed oxides, R_2O_3, with cupferron. In these procedures it will be observed that the alumina content is always determined indirectly and it is not surprising therefore that a wide variation was obtained for the alumina content of granite and diabase samples in the above mentioned investigation.

In recent publications, however, new procedures have been recommended for the direct determination of the alumina content of silica base materials on both the macro and micro scale. On the macro scale the tentative methods proposed by a British Ceramic Research Association (B.C.R.A.) Committee[2] involve the precipitation of the aluminium with 8-hydroxyquinoline followed by either direct weighing of the precipitate or the bromometric titration of the combined oxine. Solution of the sample is initially obtained by a high temperature fusion with sodium carbonate and borax. With materials having a high silica to alumina ratio, this fusion was applied after the preliminary removal of silica with hydrofluoric acid. On the micro scale MILLER AND CHALMERS[3] proposed a procedure which also used 8-hydroxyquinoline for precipitating the aluminium before weighing the precipitate. A 5 mg sample is first treated with hydrofluoric and sulphuric acids to remove silica, and the residue is then taken into solution by fusion with potassium bisulphate and extraction of the cooled melt with hydrochloric acid. Iron, titanium, vanadium and zirconium are removed together by precipitation with cupferron followed by extraction with *o*-dichlorobenzene. The aluminium is then separated from the aqueous sample solution buffered at pH 6 to 7 by extracting its acetylacetonate complex into diethyl ether. Aluminium is withdrawn from the ether layer into $6N$ hydrochloric acid, from which it is precipitated with 8-hydroxyquinoline.

MILNER AND WOODHEAD[4] recently developed a volumetric procedure for aluminium using ethylenediaminetetracetic acid which proved advantageous for the determination of this element in non-ferrous analysis after its preliminary separation by precipitating with ammonium benzoate. This technique has now been successfully extended to the determination of the alumina content of silicate rocks and refractories, and details of procedures for this determination are given in this paper.

EXPERIMENTAL

Solution technique

Various fusion procedures have been recommended for obtaining the complete solution of silicate materials. Fusion with sodium carbonate and borax is reported to be satisfactory when carried out at a temperature of 1200° C. On the microscale, however, fusion with potassium bisulphate is preferred since it eliminates the risk of loss of alumina on dissolving a sodium carbonate melt in acid. RAFTER[5] suggested a sinter technique with sodium peroxide for producing solutions of rocks and similar materials. Moreover SMALES[6] found this technique extremely satisfactory in the determination of uranium in rocks and minerals. In this work it was therefore decided to take the sample into solution by this peroxide sinter technique using a temperature of about 450-500° C. Experience soon showed, however, that for satisfactory results with this technique the particle size of the sample was of great importance. In all experiments, therefore, the samples were first crushed to a reasonably fine state in a percussion mortar, and then a suitable small amount was further ground until it was not gritty to the touch.

The peroxide sinters are readily dissolved in water, but it is necessary to make the solution acid to produce the complete solution of the material. The solubility of silica under slightly acidic conditions therefore determined the maximum weight of sample that could be safely taken. According to DAVIS AND BACON[7] the maximum concentration of silica that can be safely held in true solutino under slightly acid conditions is of the order of 0.9 mg per ml. On the assumption therefore that 100 ml volumes of solution are most convenient for any chemical treatment, the weight of sample for materials containing more than 5% of alumina was limited to 100 mg. This weight of sample was mixed with 2 g of AnalaR sodium peroxide in a platinum dish before sintering at 450-500° C for from 30-45 minutes. After allowing the sinter to cool, the best dissolving technique was found to consist of placing the platinum dish plus contents into a 250 ml squat type beaker containing 50 ml of warm distilled water and allowing the reaction to go to completion. Then the dish was removed with forceps from the beaker, whilst washing its surface with water, to give a total volume of about 100 ml of solution. Hydrochloric acid (1 : 1) was next added to make the solution just acid to litmus and a further 10 ml of concentrated acid placed in the platinum dish to dissolve any small amounts of adhering sample. The acid in the platinum was finally combined with the sample solution in the beaker.

For samples containing less than 5% of alumina, larger sample weights were desirable and this resulted in large unwieldy volumes of solution which were necessary to retain the silica completely in solution. This difficulty was overcome by carrying out a preliminary treatment with hydrofluoric and sulphuric acids on 0.5 g of sample (in a platinum dish), to remove the bulk of the silica. The sulphuric acid was finally evaporated off and the dish heated to about 1000° C for about 5 minutes. After such treatment, however, it was found impossible to mix the sample intimately with sodium peroxide before the peroxide sinter because the sample was invariably securely attached to the bottom of the dish. In consequence it was found more advantageous in this case to replace the sodium peroxide sinter by a fusion with potassium bisulphate. One gram of powdered potassium bisulphate was simply added to the platinum dish and the fusion carried out in the normal manner over a Meker burner. The most suitable technique for extracting this melt consisted of dissolving it in 30 ml of warm hydrochloric acid (1 : 2) and washing this solution into a beaker with water to give a total volume of about 100 ml of solution.

Interfering elements

It was realized that some preliminary separation of the aluminium from other sample constituents would be necessary before the EDTA titration technique could be applied. The precipitation of aluminium as its insoluble benzoate proved most advantageous for the separation of aluminium from other elements in non-ferrous metallurgical analysis. Although JEWSBURY AND OSBORN[8] reported that titanium, thorium and zirconium (+ hafnium) also produced insoluble benzoates under the conditions for the formation of aluminium benzoate, no real difficulties were encountered from these elements because they are not normal constituents of the usual non-ferrous alloys. This state of affairs does not exist with silicate materials, however, since titanium is generally a constituent and zirconium cannot be assumed to be absent. In addition the above elements form complexes with EDTA and could be expected to interfere in the aluminium titration procedure. The existence of a complex between titanium and EDTA was first reported by PRIBIL AND SCHNEIDER[9]. They observed that titanium hydroxide is not precipitated from solutions containing EDTA until they are made ammoniacal, whereas in the absence of this reagent titanium hydroxide begins to precipitate in the region of pH 2. Polarographic studies by BLUMER AND KOLTHOFF[10] have completely substantiated the existence of the titanium complexes. The complex formed by thorium and EDTA has recently been used independently by FRITZ AND FORD[11] and by TER HAAR AND BAZEN[12] for the volumetric determination of this element. Likewise the complex between zirconium and EDTA has been used by MILNER AND PHENNAH[13] and also by FRITZ AND MULDA[14] for the determination of zirconium.

Evidence for the interference of titanium was obtained in preliminary experiments on a kaolin and a firebrick sample. The proposed procedure was first applied to 100 mg portions of a pure kaolin sample which had been dried at a temperature of 105° C. After solution of the material by the peroxide sinter technique, the aluminium was then precipitated as its insoluble benzoate by the accepted method for this precipitation. On filtration and resolution of this precipitate in hydrochloric acid a figure of 37.11% was obtained for the alumina content by the EDTA titration technique. This value was in good agreement with the figure of 36.9% obtained by applying the B.C.R.A. oxine procedure to other portions of this sample. However, on applying the same benzoate-EDTA technique to a firebrick sample containing 32.50% Al_2O_3, 2.9% Fe_2O_3, 1.7% TiO_2 and silica the remainder, the figure for the alumina was 33.70% which is considerably greater than the accepted value for this constituent. This discrepancy could not arise from the presence of iron in the sample since thioglycollic acid was incorporated at the benzoate precipitation stage to prevent the precipitation of this element. It was therefore concluded that the titanium was contributing to the EDTA titration and causing the high result for the alumina. This behaviour showed the need for separating the aluminium from the elements titanium, zirconium and thorium before the benzoate precipitation of the aluminium.

Previous experience in the analysis of binary alloys of uranium with titanium[15], zirconium[16] and niobium[17] respectively, showed that cupferron was a suitable reagent for separating these elements from the uranium, especially when used in conjunction with chloroform as a solvent extraction procedure. It was realized that this technique could quite readily be applied to the removal of the titanium, zirconium and thorium from the aluminium in silicate analysis, since the behaviour of aluminium with cupferron is not unlike that for uranium. OVENSTON AND REES[18] showed that aluminium was not extracted at all from normal (N) acid solutions, whereas from $N/10$ solutions this element tended to be very slightly extracted. The results of the previous work on binary uranium alloys showed the quantitative nature of this extraction technique for titanium, zirconium etc., and further investigations were therefore considered unnecessary in this study. The solution procedure for silicate samples using sodium peroxide had to be slightly modified, however, before the cupferron extractions could be applied since the titanium existed in solution as a peroxy complex. Sulphur dioxide was bubbled through the solution for a short time to destroy this complex, but then it became necessary to boil the sulphur dioxide out of the solution and to re-oxidize any iron by the careful dropwise addition of nitric acid. In most cases extraction with two separate 20 ml portions of a solution of cupferron in chloroform (1 g of cupferron per 40 ml of chloroform) proved necessary for the separation of iron, titanium etc. present in silicate samples from the aluminium. The colour of the organic layer was found to be a useful guide in this part of the procedure; no change in the colour of this layer occurring when the extraction of the above elements was complete. The quantitative behaviour of this extraction technique was checked on a few samples by determining the titanium content of the combined organic layers. The titanium was determined absorptiometrically by its peroxy complex in sulphuric acid solutions after the wet oxidation of organic matter and in all cases complete extraction for this element was obtained. Before proceeding with the precipitation of aluminium benzoate after the cupferron extractions, it proved advisable to shake the aqueous layer with two separate 20 ml portions of pure chloroform to extract any cupferron or organic decomposition products from solution.

After the cupferron extractions the aqueous solution contains the aluminium from the sample, together with silica, sodium from the fusion and possibly various amounts of calcium, magnesium and phosphate ions. No difficulties in the aluminium determination were envisaged from silicon, sodium, calcium and magnesium since none of these elements produce a benzoate precipitate under the pH conditions needed for the formation of aluminium benzoate. In any case small amounts of any of these elements getting through to the final aluminium solution should not interfere in the EDTA titration procedure, since the stability constants for the alkali metals are low and alkaline earth elements only form stable complexes with EDTA in alkaline solutions, according to the conditions recommended in volumetric methods for these elements. However, as aluminium phosphate is precipitated at slightly lower pH values than those for aluminium benzoate, it is possible that phosphate ions may cause difficulties under some conditions. The influence of phosphate ions was therefore studied on synthetic solutions prepared by taking several portions of an aluminium solution each containing 50 mg of Al_2O_3 and adding various amounts of an ammonium phosphate solution to produce mixtures with suitable ratios of Al_2O_3 to P_2O_5. Quantitative aluminium recoveries were obtained for all ratios of Al_2O_3 to P_2O_5 from $^{250}/_1$ to $^{4}/_1$, thereafter, however, slightly low results were produced. Since silicate materials generally contain small amounts of P_2O_5, it was considered that this constituent could at the most only cause very small errors in the alumina determination.

Procedures for the determination of alumina in silicates and refractories

Reagents

All reagents should be of the highest purity and distilled water should be used throughout.

Cupferron reagent. Dissolve 10 g of cupferron in about 250 ml of cold water with stirring and remove any insoluble matter by filtration. Transfer the filtrate to a suitable separatory funnel and add dilute hydrochloric acid (1 : 1) carefully until the precipitation of the acid salt of cupferron is complete. Immediately add 400 ml of pure chloroform and shake to dissolve the precipitate. Allow the layers to separate and then transfer the organic layer to a suitable flask. Store if necessary in an ice bath, but early use of this reagent is strongly recommended.

Ammonium benzoate wash solution. Dissolve 10 g of ammonium benzoate in water with warming. Then add 20 ml of glacial acetic acid and dilute to 1 litre with water.

Standard iron solution, 0.1 molar. Dissolve 5.585 g of specpure iron in 20 ml of hydrochloric acid (sp.gr. 1.16) and then oxidize with a few ml of nitric acid. (sp.gr. 1.42). Dilute this solution to 1 litre with water.

Ethylenediaminetetraacetic acid solution, 0.1 molar. Dissolve 37.23 g of the disodium salt of EDTA in water and dilute to one litre. Determine the exact molarity of this solution by the following procedure: - transfer 20 ml of the standard 0.1*M* iron solution to a 150 ml beaker and then add 25 ml of the EDTA solution. Dissolve 3 g of ammonium acetate in this solution and then add ammonium hydroxide (1 : 4) to adjust the pH to a value of 6 using a direct reading pH meter. Add 0.2 g of salicylic acid and titrate with the standard iron solution whilst stirring with a glass rod. At the end-point the colour of the solution changes from yellow to brown.

$$\text{Molarity of EDTA} = \frac{(20 + \text{back titration in ml}) \times 0.1}{25}$$

Procedure I for samples containing more than 5% Al_2O_3

Weigh 100 mg of finely ground sample, which has previously been dried at 110° C for approximately 1 hour, into a platinum dish with a capacity of about 40 ml. Then add 2 g of sodium peroxide, mix thoroughly with the sample using a platinum rod, and heat the dish and contents for 30-45 minutes in a muffle furnace controlled in the temperature range from 450-500° C. After cooling, place the dish into a 250 ml squat type beaker containing 50 ml of warm distilled water and allow the melt to dissolve in the water. When dissolving action has ceased, remove the dish with forceps washing well with about 50 ml of water and combining the washings with the sample solution. Then add hydrochloric acid (1 : 1) dropwise from a pipette to make the sample solution just acid to litmus. Place 10 ml of hydrochloric acid (sp.gr. 1.16), into the platinum dish to dissolve any traces of adhering material and then add to the sample solution in the beaker, washing in with a small amount of water. Pass gaseous sulphur dioxide through the solution for a few minutes to break down any titanium peroxide complex— the colour of the solution often serves as a good indication for the completion of this reaction for samples containing more than trace amounts of titanium. Then place a bumping rod in the solution and heat to boiling. Continue boiling to drive off the excess sulphur dioxide and then add the minimum amount of nitric acid (sp.gr. 1.42) dropwise to re-oxidize any iron in the sample (again the colour of the solution often serves as a good indication of the progress of the oxidation). Continue boiling for a short time to drive out any oxides of nitrogen and then cool down to the temperature of an ice bath.

Transfer the cooled sample solution to a 250 ml separating funnel, add 20 ml of the cupferron reagent in chloroform and shake gently for about 2 minutes. Allow the two layers to separate and transfer the organic layer to a beaker, washing through with 5 ml of chloroform. Repeat this extraction procedure with a further 20 ml portion of the cupferron reagent and observe the colour of the organic layer after allowing the two layers to separate. If the colour has not changed, the first extraction removed the iron, titanium, etc., from the aqueous layer and the cupferron extractions can be discontinued. If the colour has changed, continue extracting with the cupferron reagent, but in most cases extraction with two 20 ml portions will be sufficient. Next add 20 ml of pure chloroform to the separating funnel and shake for about 2 minutes. Discard the organic layer washing through with 5 ml of chloroform. Repeat this extraction with a further 20 ml of pure chloroform to remove as much cupferron or its oxidation products as possible from the aqueous solution.

Transfer the aqueous solution to a 400 ml squat type beaker, washing the separating funnel walls with water and bring the solution to the boil. Continue boiling to expel the chloroform, and then dilute the solution to a volume of about 200 ml by the addition of hot distilled water, if necessary. Next precipitate aluminium benzoate by adding 1 ml of thioglycollic acid (90%) followed by 15 ml of a hot solution containing 1 g of ammonium chloride, 2 g of ammonium acetate, and 3 g of ammonium benzoate. Then add ammonium hydroxide (1 : 1) dropwise to the appearance of a faint permanent white precipitate and boil the solution at this stage for about 2 minutes. Next adjust the pH of the solution to a value of about 4 by adding diluted ammonium hydroxide (1 : 4) and using narrow range pH papers. Boil the solution for a further 2 minutes and allow to stand warm for approximately 30 minutes, before filtering through a Whatman No. 541 paper. Wash the precipitate with the hot ammonium benzoate wash solution and then wash from the filter paper with hot water into a 250 ml squat beaker. Dissolve traces of precipitate from the filter paper by pouring 20 ml of hot hydrochloric acid (1 : 1) over it followed by further washing with hot water. Collect all solutions and washings in the same beaker and heat if necessary to dissolve completely the aluminium benzoate precipitate. The volume of solution at this stage should be of the order of 100 ml.

To the aluminium solution, add sufficient of the EDTA solution to give about a 10% excess of reagent over that needed to complex the aluminium and then add ammonium hydroxide (1 : 1) until the solution is just alkaline to methyl red. Boil this solution for 2 minutes, then cool, add 3 g of ammonium acetate and adjust the pH to 6.5 with a direct reading pH meter by adding a weak ammonium hydroxide or acetic acid solution. Next add approximately 0.2 g of salicylic acid and back titrate the excess of EDTA with the standard iron solution until the brown iron salicylate colour just persists. For solutions containing less than 30 mg of aluminium use a 0.02*M* EDTA solution with 0.02*M* standard iron solution for the back titration. For solutions with more than 30 mg of aluminium use 0.1*M* solutions of both EDTA and ferric iron.

Calculate the aluminium content from the expression

1 ml 0.1*M* EDTA = 2.697 mg of aluminium = 5.095 mg Al_2O_3

Procedure II for samples containing less than 5% Al_2O_3

Weigh 500 mg of finely ground material, which has previously been dried at 110° C for approximately 1 hour, into a platinum dish with a capacity of 40 ml. Moisten the sample with water, then add 5 drops of sulphuric acid (sp.gr. 1.84) followed by about 10 ml of hydrofluoric acid (40% w/w). Warm this solution and evaporate to fumes of sulphuric acid using radiant heaters. Cool slightly, add a further 2 to 3 ml of hydrofluoric acid (40% w/w) and reheat to fumes of sulphuric acid. Continue heating until the acid fumes cease to be evolved and then gradually raise the temperature of the dish plus contents to the region of 1000° C and maintain at this value for approximately 5 minutes. Allow to cool, add 1 g of potassium bisulphate and carry out a bisulphate fusion by heating over a Meker burner. Allow the bisulphate melt to cool and extract with 30 ml of (1 : 2) hydrochloric acid. Transfer the solution to a 250 ml squat beaker, washing in with water to give a volume of about 100 ml of solution. Bring this solution to the boil and oxidize any ferrous iron by the addition of a few drops of nitric acid (sp.gr. 1.42). Continue boiling for a short time to expel any oxides of nitrogen and then cool down to the temperature of an ice bath. Proceed with the cupferron extractions and complete the determination as in Procedure I using 0.02*M* EDTA and iron solutions for the titration.

Results and conclusions

These procedures were tested by applying them to analysed silicate rocks and refractories and the alumina results are compared against the reported figures for these samples in Table I.

In rock analysis it will be observed that the results by our procedure for the feldspar and flint clay samples confirm those obtained by MILLER AND CHALMERS on the micro scale. This agreement may lend support to the suggestion that the

TABLE I

DETERMINATION OF ALUMINA IN SILICATE ROCKS AND REFRACTORIES

Silicate Rocks	Composition % SiO_2	Fe_2O_3	FeO	TiO_2	P_2O_5	CaO	MgO	MnO	K_2O	Na_2O	Procedures I and II	Al_2O_3 Classical procedure	Micro method of MILLER AND CHALMERS
1. Feldspar No. 70*	67	0.03	—	<.01	0.01	0.07	0.01	<.01	—	—	17.80 17.70 17.86	18.03	17.86 17.71
2. Feldspar No. 99*	69	0.07	—	0.02	0.14	0.36	0.05	<.01	—	—	18.85 18.65	19.06	18.94 18.77
3. Flint Clay No. 97*	43	0.98	(total) (iron)	2.38	0.08	0.10	0.26	<.01	0.54	0.33	38.40 38.18 38.11	38.77	38.23 38.43 38.43
4. Granite G1**	72.2	0.94	1.00	0.26	0.10	1.42	0.39	0.03	5.51	3.26	14.38 14.27 14.40	14.44 → 13.94+ ± 0.54	
5. Diabase W 1**	52.25	1.85	8.51	1.09	0.13	10.95	6.52	0.19	0.71	2.05	14.97 14.88	15.23 → 14.72+ ± 0.94	
Silicate Refractories													
6. Silica Brick No. 102*	93.94	0.66	(total) (iron)	0.15	0.025	2.29	0.21	.005	0.29	0.06	1.89 1.89 1.90	1.96	
7. Silica Brick No. 2***											1.10 1.12 1.14		1.14 ± .02 (BCRA figures)
8. Silica Brick No. 1***		2.9		1.7							32.60 32.55		32.50 ± 0.17 (BCRA figures)
9. Sillimanite****	41.27	0.63		1.06	0.18	0.80	0.73	—	0.55	0.30	54.37 54.56	54.40 ±.29	
10. Synthetic sample (0.1g. of silica brick No. 102 + 0.4g. of SiO_2)											0.395 0.385	0.39	

* U.S. Bureau of Standards sample.

** Samples employed in a co-operative Investigation of Precision and Accuracy in the Analysis of Silicate Rocks.

*** Samples used in the investigation of the BCRA Committee.

**** Sample used in Glass Technology study[19]

+ Revised figures[20].

alumina figures for these samples by classical procedures are inclined to be slightly high. On the other hand this state of affairs may arise from the use of similar extraction techniques in both these methods for removing interfering elements from the aluminium with consequently comparable small losses of the aluminium. With the Granite and Diabase samples the position is rather obscure as these samples were not analysed for alumina by MILLER AND CHALMERS. Our results are lower than the original alumina figures obtained by classical procedures in a co-operative investigation, but higher than recently revised figures for this constituent. In the analysis of refractory materials good agreement was obtained between the results by our procedure and those by the BCRA 8-hydroxyquinoline methods. With the Bureau of Standards Silica Brick No. 102, however, the reported alumina figure obtained by classical methods was again slightly higher than our result. The synthetic sample No. 10 was introduced to confirm that Procedure II was also applicable to samples containing less than 1% of alumina.

Procedure I is fairly rapid and suitable for routine analysis as under favourable conditions it is possible to complete the alumina determinations on a suitable batch of samples in about one day. This state of affairs does not apply, however, with Procedure II because the preliminary treatment with hydrofluoric and sulphuric acids is rather time consuming and cannot be unduly hastened. Fortunately the samples do not require much attention during this treatment and the chemist is free for other work.

ACKNOWLEDGEMENT

Thanks are due to Dr. C. C. MILLER, Miss V. DIMBLEBY and Mr. B. BAGSHAWE for generously supplying several of the analysed samples.

SUMMARY

New procedures have been developed for determining the alumina contents of silicate material (rocks and refractories). The material is first taken into solution by a peroxide sinter technique, followed by dissolving the sinter in warm water and the addition of sufficient hydrochloric acid to render the solution acid to litmus. A different technique is used for silicates containing less than 5% alumina. The majority of the silica is first removed by treating with hydrofluoric-sulphuric acids and the residue is fused with potassium bisulphate. Extractions with cupferron are next employed to remove iron, titanium, zirconium etc., and the aluminium is subsequently separated from other sample constituents by precipitating as its insoluble benzoate. After filtration the aluminium benzoate is dissolved in hydrochloric acid and the aluminium concentration determined volumetrically with ethylenediaminetetraacetic acid.

RÉSUMÉ

De nouveaux procédés ont été établis pour la détermination de l'aluminium dans divers silicates (roches et matières réfractaires). La substance à analyser est désagrégée par la méthode au peroxyde; on dissout ensuite dans l'eau chaude et on acidifie par l'acide chlorhydrique jusqu'au virage du tournesol. Une technique différente est utilisée pour des silicates renfermant moins de 5% d'aluminium.

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La plus grosse partie de la silice est d'abord éliminée par traitement aux acides fluorhydrique et sulfurique, le résidu est fondu au moyen de bisulfate de potassium. Des extractions au cupferron sont ensuite effectuées pour éliminer le fer, le titane, le zirconium, etc., l'aluminium peut alors être séparé des autres constituants par précipitation comme benzoate. Après filtration, le benzoate d'aluminium est dissous dans l'acide chlorhydrique et la teneur en aluminium est déterminée volumétriquement par l'acide éthylènediaminotétraacétique.

ZUSAMMENFASSUNG

Es werden neue Verfahren vorgeschlagen zur Bestimmung von Aluminium in verschiedenen Silikaten (Gesteine und Feuerfeste-Gesteine). Die zu analysierende Substanz wird einem Aufschluss nach der Peroxydmethode unterzogen. Dann wird sie in heissem Wasser gelöst und man säuert mit Salzsäure an bis zum Umschlagspunkt von Lackmus. Eine verschiedene Arbeitsweise wird angewendet für Silikate, welche weniger als 5% Aluminium enthalten. Der grösste Teil des Siliziums wird vorher eliminiert durch eine Behandlung mit Fluorwasserstoff- und Schwefelsäure; der Rückstand wird dann mit Kaliumbisulfat geschmolzen. Nachher wird mit Kupferron extrahiert, um das Eisen, das Titan, das Zirkonium usw. abzutrennen. Das Aluminium kann nun von den restlichen Bestandteilen abgetrennt werden durch Ausfällung als Benzoat. Nachdem man filtriert hat, wird das Aluminiumbenzoat in Salzsäure gelöst und der Gehalt an Aluminium volumetrisch mit Ethylendiaminotetraessigsäure bestimmt.

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SUR LA THERMOGRAVIMÉTRIE DES PRÉCIPITÉS ANALYTIQUES
LXIV. DOSAGE DU RHODIUM*

par

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On a, jusqu'ici, proposé de faire la gravimétrie du rhodium en pesant le métal, après refroidissement dans l'azote. La précipitation peut s'effectuer à l'aide des réactifs suivants:

Thionalide,
Mercapto-2 benzoxazole,
Acide thiobarbiturique.

A. Rhodium métallique

L'échantillon utilisé, en grains blanc d'argent, de diamètre inférieur à un millimètre, provient de la firme Heraeus (Allemagne). Si l'on en chauffe 260 mg en creuset ouvert, linéairement, à raison de 200°/heure, la courbe inscrite reste horizontale jusqu'à 662° au moins.

Le gain d'oxygène se fait ensuite proportionnellement à la température (et par suite, au temps). Il atteint 13 mg à 946°, limite de l'expérience (Fig. 1); les grains sont devenus noirs extérieurement; il est probable, comme divers auteurs l'ont noté depuis BERZELIUS, qu'ils se sont recouverts d'une couche d'oxyde Rh_2O_3, mais la transformation est loin d'être intégrale à cette température et avec cette vitesse de chauffe. Le poids final est, en effet 273.9 mg au lieu de 321.8 mg (calculé).

Si maintenant, on considère le rhodium provenant de la destruction des complexes internes qu'il fournit avec le thionalide, le mercapto-2 benzothiazole, l'acide thiobarbiturique, il est tout à fait surprenant de voir que le métal résiste à l'oxydation, tout au moins, jusqu'à 1000°. Ce fait suggère l'abandon de l'emploi de l'hydrogène, puis de l'azote pour effectuer une éventuelle réduction, puis, le refroidissement, car cette complication, parfaitement inutile est en désaccord avec l'enregistrement des courbes de thermolyse.

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* Pour LXIII (Platine), voir *Anal. Chim. Acta,* 10 (1954) 443.

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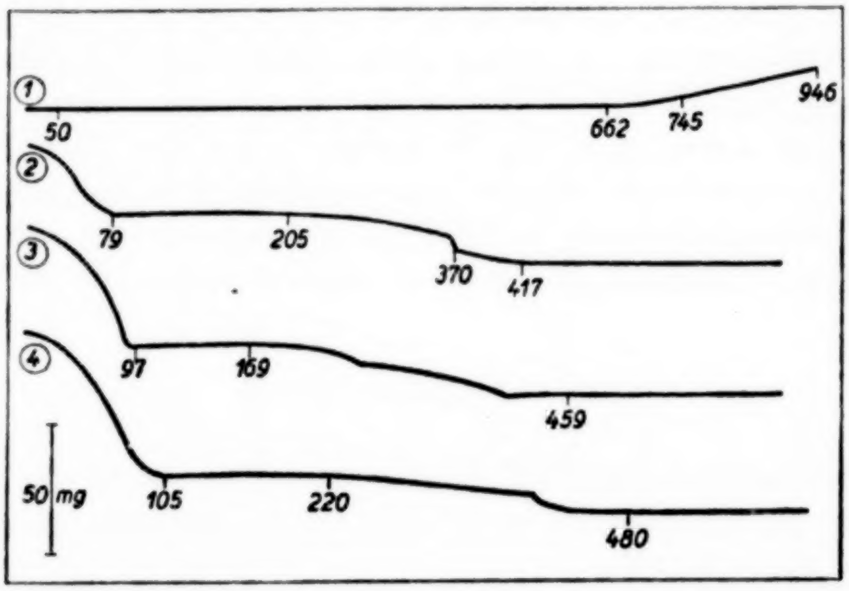
B. Précipitation avec le thionalide

Le précipité orange de formule $Rh(C_{12}H_{10}OSN)_3$, exempt de chlorure de rhodium s'obtient suivant la technique décrite par KIENITZ et ROMBOCK[1]. Ces auteurs ont surtout pratiqué un dosage iodométrique de l'excès de thionalide, mais, la méthode peut servir à la gravimétrie et à la microgravimétrie. La courbe 2 montre, en effet, qu'après le départ d'humidité, le précipité se conserve anhydre et avec un poids constant de 79° à 250°, avec la vitesse de chauffe indiquée. Après cette température, la matière organique se détruit, avec chute brusque vers 370°; on peut compter sur un poids constant à partir de 417°; comme nous l'avons dit, le palier se maintient horizontal jusqu'à 1000°; le métal résiduel est gris et présente l'aspect d'une éponge; nous préconisons le complexe avec le thionalide pour le dosage automatique du rhodium, avec le poids moléculaire 751.69 et le facteur analytique 0.1369. Nous avons pu effectuer ce dosage sur la thermobalance jusqu'à 6.5 mg de rhodium.



Courbes de thermolyse du rhodium et de ses dérivés.
Fig. 1. Rhodium métallique;
Fig. 2. Composé avec le thionalide;
Fig. 3. Composé avec le mercapto-2 benzoxazole;
Fig. 4. Composé avec l'acide thiobarbiturique.

C. Précipitation avec le mercapto-2 benzoxazole

Le précipité de formule $Rh(C_7H_4OSN)_3$ s'obtient aisément à partir du chlorure $RhCl_3$ en suivant les indications de HAINES ET RYAN[2].

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La courbe 3, tracée avec ce précipité ressemble beaucoup à la précédente mais il est prudent de ne pas dépasser 150° pour le dosage automatique du complexe interne dont le palier s'étend, après départ d'eau, de 92° à 155°; la destruction de la matière organique s'effectue lentement et le rhodium métallique apparaît pur vers 459°. Le poids moléculaire du dérivé vaut 553.39 avec le facteur 0.1859. La méthode nous a permis encore de descendre jusqu'à 6.5 mg de rhodium; elle nous paraît aussi recommandable que la précédente du point de vue insolubilité et traitement du précipité, mais le facteur analytique est un peu plus élevé dans le cas présent.

D. Précipitation avec l'acide thiobarbiturique

Le précipité formé, de couleur brun-chocolat, suivant CURRAH, MCBRYDE, CRUIKSHANK ET BEAMISH[3] en traitant le rhodium(III) hexachlorure de sodium par l'acide thiobarbiturique, en milieu acide, nous paraît quantitatif mais non défini. Il renferme 33.60% de rhodium; ainsi, une expérience faite avec 41.27 mg de ce précipité sec donne 13.87 mg de métal, ce qui ne s'accorde pas avec les formules essayées. La méthode ne peut donc pas servir pour le dosage automatique mais on peut l'utiliser pour peser le métal qui apparaît pur vers 480°. Le précipité lui-même, de nature inconnue, se maintient stable entre 105° et 220° en moyenne.

TABLEAU RÉCAPITULATIF

Le tableau récapitulatif habituel fournit les formes de pesée, les limites de température que nous conseillons et les deux formes indiquées par un astérisque pour le dosage automatique.

Réactifs	Formes de pesée	Limites de température
* Thionalide	$Rh(C_{12}H_{10}OSN)_3$	79-250°
Thionalide	Pt	au-dessus de 417°
* Mercapto-2 benzoxazole	$Rh(C_7H_4OSN)_3$	92-150°
Mercapto-2 benzoxazole	Pt	au-dessus de 459°
Acide thiobarbiturique	Pt	au-dessus de 480°

RÉSUMÉ

Les auteurs montrent que le rhodium n'est pas aussi oxydable qu'on l'avait cru jusqu'ici. On peut peser le métal vers 550°. Ils fournissent deux nouvelles formes de pesée, à l'aide des complexes internes donnés avec le thionalide et le mercapto-2 benzoxazole.

Bibliographie p. 141.

SUMMARY

The authors show that rhodium is not so easily oxidized, as one has up to now supposed. It is possible to weigh the metal up to 550°. They propose 2 new forms of weighing with the help of the internal complexes which can be formed with thionalide and mercapto-2-benzoxazole.

ZUSAMMENFASSUNG

Die Autoren zeigen, dass das Rhodium nicht so leicht oxydiert wird, wie man bisher angenommen hat. Das bis gegen 550° erhitzte Metall kann gewogen werden. Sie schlagen zwei neue Arten für die Wägung vor mit Hilfe der inneren Komplexe, welche mit dem Thionalid und dem Mercapto-2-benzoxazol gebildet werden.

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CHROMATOGRAPHY ON PAPER IMPREGNATED WITH ION EXCHANGE RESINS
A PRELIMINARY REPORT

by

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The advantages of a paper equipped with ion exchange groups were stated by WIELAND AND BERG[1] who, like numerous other workers[2], conferred ion exchange properties to filter paper by chemical reactions such as careful oxidation.

Although an ion exchange paper may be equipped even with sulphonic or quarternary ammonium groups, it would not be in any relation to the ion exchange resins now employed in analytical chemistry such as Dowex and Amberlite resins since cross-linking and diffusion characteristics could not be imitated by attaching functional groups to the cellulose network.

For this reason we have tried for several years to obtain a filter paper in which the usual resins are incorporated. We wish to thank the Permutit Company for kindly putting a paper at our disposition which was prepared by polymerising the resin on the paper. However, during this process the paper looses its porosity and chromatographic development is rendered impossible.

Several attempts to persuade English and French paper manufacturers to include colloidal aggregates of Dowex-50 as filler in ordinary filter paper were so far unsuccessful.

We have recently found a laboratory method by which filter paper can be impregnated with resins with sufficient uniformity to yield a paper suitable for chromatography. All that is required is to prepare a suspension of the colloidal form of the ion exchange resin and to pass paper strips through this suspension as uniformly as possible and to dry the paper afterwards in air by placing it on another sheet of filter paper so as to avoid irregularities due to running of the suspension.

The paper so produced has almost the appearance of untreated filter paper but is rougher to the touch.

We shall now describe some experiments performed with ion exchange resin papers which serve to indicate some practical applications.

Separation of rare earths

A Dowex-50 paper was prepared by washing Dowex-50 colloidal aggregates with HCl, NaCl, again with HCl and finally with distilled water. A suspension of about one volume of wet resin with two volumes of distilled water was prepared and excess ammonia added to convert the resin to the ammonium form. Whatman No. 1 strips 30 cm long and 4 cm wide were dipped into the suspension in the same manner as photographic film is developed by running it through the solution. Before each paper strip the suspension is thoroughly stirred. The papers after impregnation are quickly placed on pieces of Whatman No. 1 paper which absorbs the excess liquid immediately. The strips are then left to dry at room temperature overnight.

To establish the correct concentration and pH for rare earth separations, preliminary work was carried out with a 'didymium nitrate' preparation. The pH and citrate concentration optima will be different to those of the analogous column of resin as the ratio of resin phase to liquid phase is altered by the presence of the porous paper which increases the amount of liquid phase in contact with the resin. Under optimum conditions the didymium nitrate yielded at least four well separated spots which have not yet been identified; one is probably lanthanum.

Thus for examining the efficiency of the paper we resorted to an artificial mixture of three rare earths which are available in a reasonably pure state namely lanthanum, cerium and yttrium. Fig. 1 shows the separation of these three with 3% citrate at pH 3 as eluant. The rare earth nitrates were dissolved in a few drops of the eluant and so spotted on the paper. The two strips were prepared on different days and run for about two hours each. The spots are revealed by spraying the paper after drying on a steam bath with alcoholic ammoniacal 8-hydroxyquinoline and viewed under ultra-violet light.

Partition chromatography on ion exchange resin paper

An untreated paper strip and one impregnated with the hydrogen form of Dowex-50 were both spotted with a mixture of Co, Cu and Fe(III) chlorides and developed with acetone-HCl-water for one hour. As seen in Fig. 2 there is hardly any difference between the separation on plain and impregnated paper. Thus, at least in this solvent, one must consider the influence of ion-exchange on partition chromatography as negligible.

Separation with anion exchange resin paper

KRAUS AND MOORE[3] have published a thorough study of the separation of the transition elements on Dowex-1 columns using aqueous HCl at various concentrations as eluant. We have tried to repeat this work on paper but were somewhat handicapped by the fact that the only anion exchange resin available was Dowex-2 (200-400 mesh). Impregnation with such large particles is of course

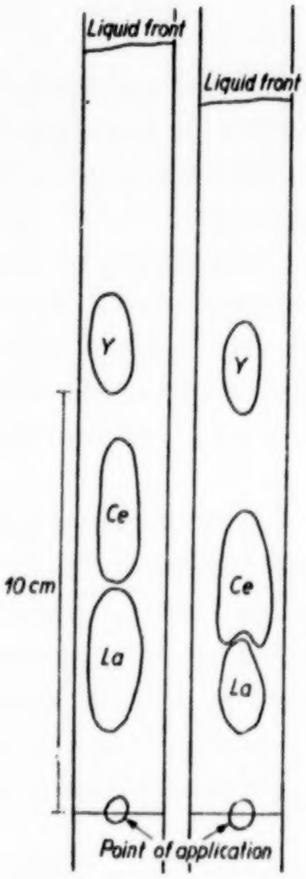
Liquid front
Liquid front
Y
Ce
La
Y
Ce
La
10 cm
Point of application

Fig. 1

Fig. 1. Separation of a mixture of Y, Ce and La on Dowex-50 paper (ammonium form) with 3% citrate at pH 3 for 2 h.

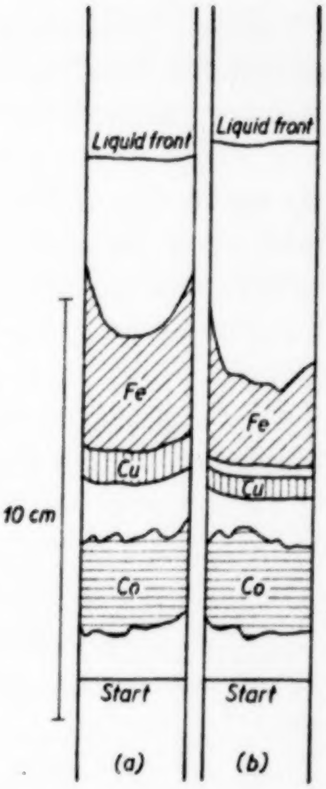
Liquid front
Liquid front
Fe
Cu
Co
Fe
Cu
Co
10 cm
Start
Start
(a)
(b)

Fig. 2

Fig. 2. Partition chromatography with ion exchange paper.
(a) untreated Whatman No. 1 paper
(b) Dowex-50 (hydrogen form) paper.

Both were developed with a mixture of acetone/HCl/water (90 : 5 : 5) for 1 h.

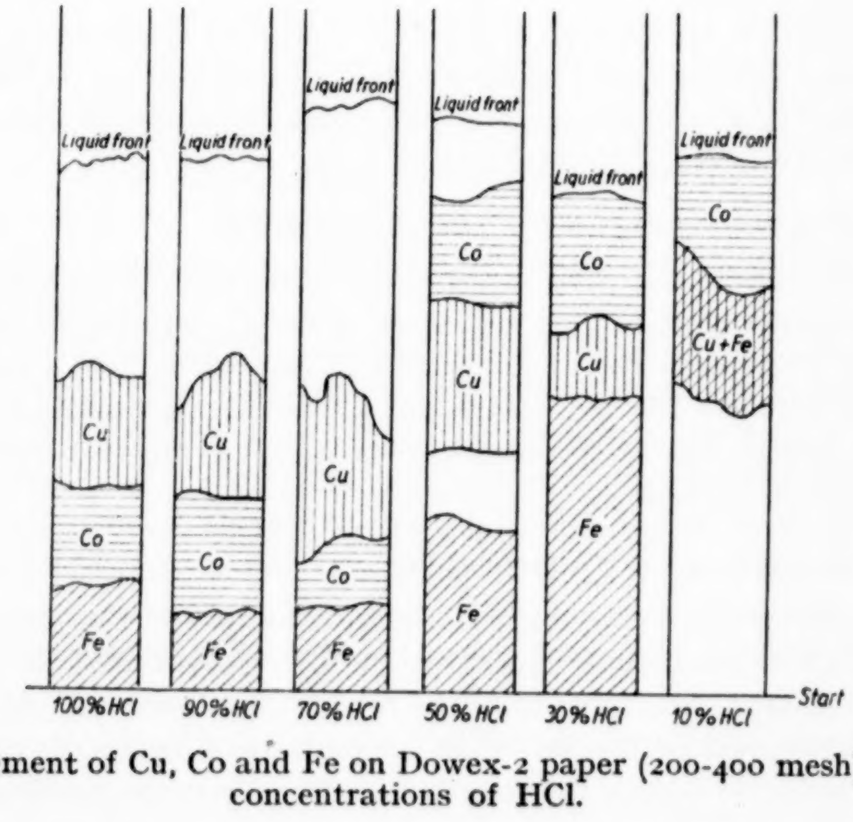
Liquid front
Liquid front
Liquid front
Liquid front
Liquid front
Liquid front
Cu
Co
Fe
Cu
Co
Fe
Cu
Co
Fe
Co
Cu
Fe
Co
Cu
Fe
Co
Cu+Fe
Start
100% HCl
90% HCl
70% HCl
50% HCl
30% HCl
10% HCl

Fig. 3. Movement of Cu, Co and Fe on Dowex-2 paper (200-400 mesh) with various concentrations of HCl.

not as uniform as is desired, however, we could repeat one aspect of the work of KRAUS AND MOORE namely the observation of the sequence changes with variation of the HCl concentration used as eluant. The chromatograms for several HCl concentrations are shown in Fig. 3. These agree essentially with the results obtained by KRAUS AND MOORE for the same elements.

SUMMARY

Ion exchange papers were prepared by dipping paper in suspensions of colloidal resin aggregates. These papers were used for the separation of rare earths, partition chromatography and the study of the elution sequence of some transition metals.

RÉSUMÉ

Des papiers échangeurs d'ions ont été préparés par immersion du papier dans une suspension colloïdale de résine. Ces papiers permettent: la séparation des terres rares, l'étude des séquences d'élution de quelques métaux de transition, et la chromatographie de partage.

ZUSAMMENFASSUNG

Ionenaustauschende Papiere wurden präpariert durch Eintauchen des Papiers in einer kolloïdalen Suspension von Harz. Diese Papiere wurden für Abtrennung der seltenen Erden, die Untersuchung der Elutionssequenzen von einigen Metallen und die Verteilungschromatographie untersucht.

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PAPER CHROMATOGRAPHY OF INORGANIC IONS
X. A STUDY OF RHENIUM, TECHNETIUM AND SOME OTHER NON-METALS

by

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The behaviour of numerous ions in a number of solvents has been described in parts 1,7 and 8 of this series[1,2,3]. The only ions not studied with butanol/HCl, butanol/HNO_3 or butanol/NH_4OH were the anions of groups VIb and VIIa of the periodic table and the transuranic elements. In this paper we propose to discuss the paper chromatography of the anions SO_4^{-2}, SeO_3^{-2}, TeO_3^{-2}, TcO_4^- and ReO_4^- in acid and alkaline solvents.

Selenite and tellurite have already been separated by BURSTALL and coll.[4] and their separation from Po was described by LEDERER[5] (in butanol/1*N* HCl R_F of $TeO_3^{-2} = 0.18$, and $SeO_3^{-2} = 0.67$ with reference to the butanol front).

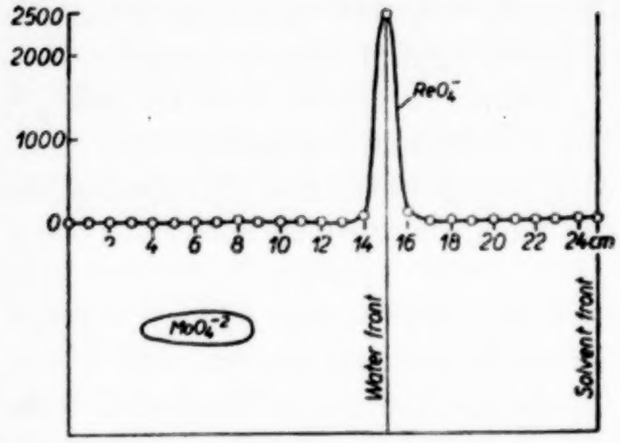
No paper chromatographic studies have yet been recorded of compounds of technetium and rhenium.

The study of these two elements was carried out with radioactive isotopes; carrier-free ^{99}Tc (5.9 h) and ^{186}Re (92.8 h) with some inactive carrier being employed. Since the detection of SO_4^{-2} in such solvents as butanol/HCl is rather difficult, carrier-free ^{35}S was included in this work so as to complete the data on the paper chromatography of inorganic ions. The separation SO_4^{-2}-PO_4^{-3} was also studied at the tracer level using carrier-free $H_3{}^{32}PO_4$.

R_F *values in butanol shaken with* 1*N HCl*

Both pertechnetate and perrhenate travel with the water front in butanol/1*N* HCl and are thus well separated from numerous ions such as MoO_4^{-2}(R_F 0.5) and Mn^{+2}(R_F 0.1).

Figs. 1 and 2 show the radioactivity distribution on the paper when pertechnetate and perrhenate ions are developed on the same sheet with inactive molybdate (detected with H_2S). In all studies of Tc relatively short chromatograms had to be carried out as the short half-time of ^{99}Tc (the only isotope available to us) did not permit detection after development overnight.



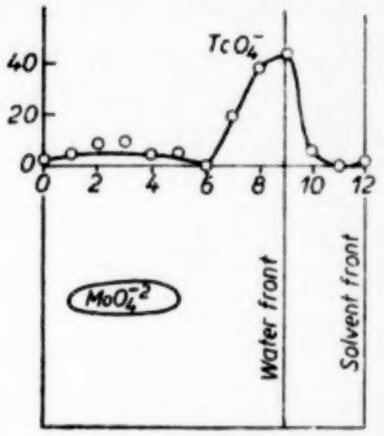


Fig. 1. Chromatogram of NH_4ReO_4 and $(NH_4)_2MoO_4$ on the same sheet with butanol saturated with 1*N* HCl. Time of development 17 h.

Fig. 2. Chromatogram of NH_4TcO_4 and $(NH_4)_2MoO_4$ on the same sheet of paper with butanol saturated with 1*N* HCl. Time of development 4 h.

Fig. 3 shows the activity distribution of a mixture of sulphuric acid (carrier-free ^{35}S and phosphoric acid (carrier-free ^{32}P) and the activity distribution of sulphuric acid alone. The separation SO_4^{-2} — PO_4^{-3} is radiochemically complete.

R_F values in butanol shaken with 1.5*N* HNO_3

In a previous publication[5] we have pointed out that the difference in R_F values between butanol/HCl and butanol/HNO_3 can be explained by considering the complex formation of the ion chromatographed with the acid in the solvent. Thus Bi^{+3} and Cd^{+2} for example which form complexes with HCl travel faster

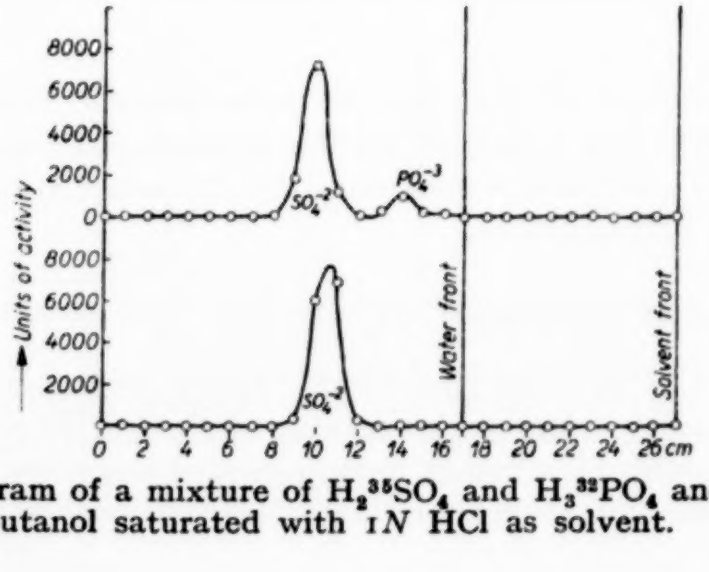
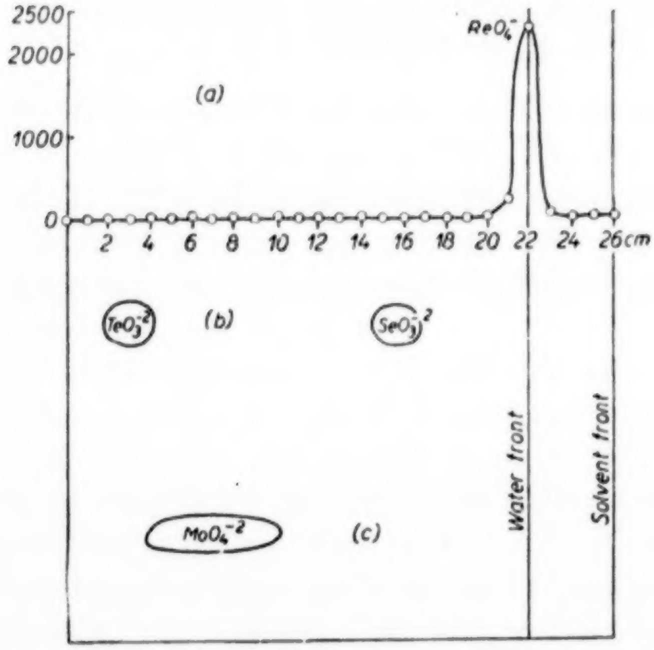


Fig. 3. Chromatogram of a mixture of $H_2{}^{35}SO_4$ and $H_3{}^{32}PO_4$ and of $H_2{}^{35}SO_4$ on the same sheet with butanol saturated with 1*N* HCl as solvent.

in butanol/HCl than in butanol/HNO_3, while UO_2^{+2} travels faster in butanol/-HNO_3 owing to the formation of the well-known uranyl nitrate complex.

According to these considerations the R_F values of anions such as MoO_4^{-2}, SeO_3^{-2} and TeO_3^{-2} should not be influenced by a change in the acid present as no complexes are formed but if anything only by a change in the concentration of the acid (as this governs the degree of ionisation of the acids, molybdic etc.) and hence their extractability into the butanol.

These arguments were confirmed experimentally with MoO_4^{-2}, SeO_3^{-2}, TeO_3^{-2}, ReO_4^- and TcO_4^- all having the same R_F values in butanol shaken with HNO_3 as in butanol shaken with HCl. Figs. 4 and 5 show the position of the spots and the radioactivity distribution in the case of radioelements. These results are of importance when selecting a solvent for the separation of cations from anions.



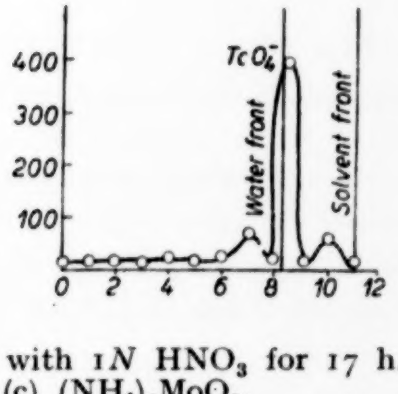


Fig. 4. Chromatogram developed with butanol shaken with 1N HNO_3 for 17 h. (a) NH_4ReO_4 . (b) mixture of SeO_3^{-2} and TeO_3^{-2} (c) $(NH_4)_2MoO_4$.

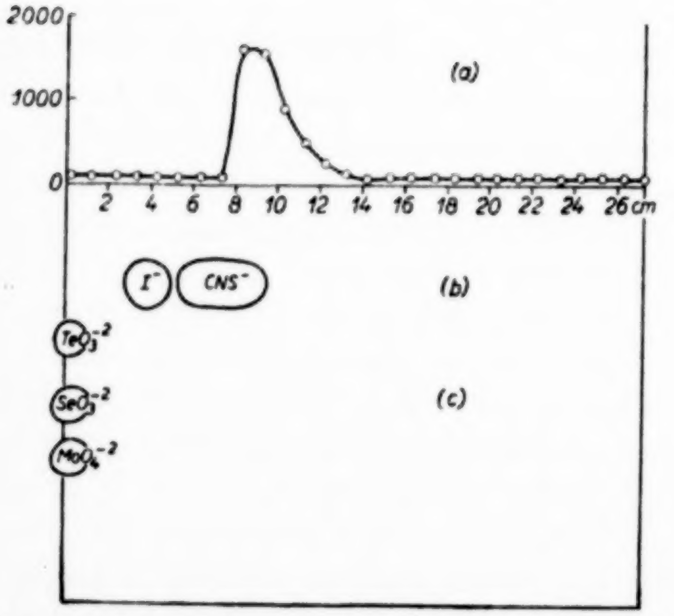
Fig. 5. NH_4TcO_4 developed with butanol shaken with 1N HNO_3 for 4 h.

For example Mo — Cd have a very small R_F difference in butanol/HCl but a large difference in butanol/HNO_3.

R_F values in butanol shaken with 1.5N NH_4OH

In another paper[6] we have recorded the R_F values of nineteen common anions in butanol/NH_4OH. Polyvalent anions all stay at R_F 0 while monovalent anions move at different speeds. The fastest anion recorded was CNS^- which is followed by I^-. As perrhenate and pertechnetate are both monovalent anions and as Tc is only known in tracer quantities, it was considered of interest to compare these with those ions previously examined.

The anions I^-, CNS^-, ReO_4^- and TcO_4^- were run in the same sheet and it was observed that the reproducibility of R_F values in butanol/NH_4OH depends largely on the room temperature and lower R_F values were recorded for I^- and CNS^- in this work than previously when the chromatograms were developed in the summer in Sydney (Australia) without air-conditioning. However, the sequence of ions was unchanged in all experiments. Figs. 6 and 7 show ReO_4^-, CNS^- and I^- developed overnight and TcO_4^-, ReO_4^-, I^- and CNS^- developed for four hours. The sequence of the spots is TcO_4^- (fastest), ReO_4^-, CNS^- and I^- (slowest). As the R_F values of MoO_4^{-2}, SeO_3^{-2} and TeO_3^{-2} had never been recorded with this solvent, they were also run overnight and found to stay at R_F 0. Thus of the inorganic anions so far examined TcO_4^- and ReO_4^- are the most solvent soluble. Unfortunately MnO_4^- is instantaneously reduced by the paper and hence a comparison with Tc and Re impossible. As evident from Fig. 7 the separation of Re and Tc is incomplete in four hours but the R_F difference is sufficient to allow a complete separation on longer development as may be of interest for the identification of Tc isotopes with a longer half-time such as ^{97}Tc (90 days).



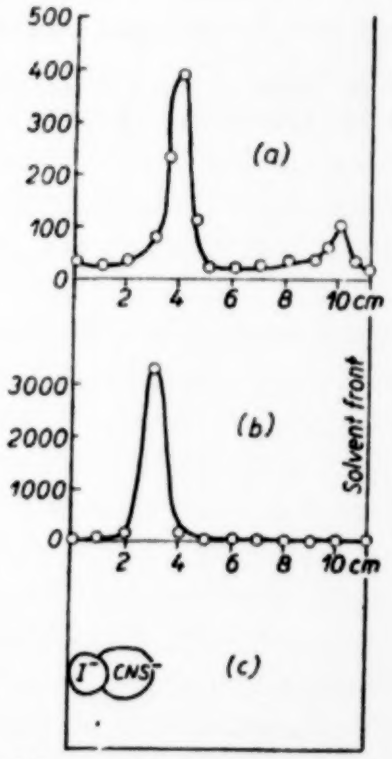


Fig. 6. Chromatogram developed with butanol saturated with 1.5*N* NH_4OH for 17 h.
(a) NH_4ReO_4 (b) mixture of KI and NH_4CNS
(c) tellurite, selenite and molybdate

Fig. 7. Chromatogram developed with butanol saturated with 1.5*N* NH_4OH for 4 h.
(a) NH_4TcO_4, the peak near the liquid front appears to be an impurity
(b) NH_4ReO_4
(c) mixture of KI and NH_4CNS

References p. 150.

SUMMARY

The movement of pertechnetate, perrhenate, tellurite, selenite and several other anions was examined with butanol shaken with HCl, HNO_3 or NH_4OH. Separations of Re-Tc, PO_4^{-3}-SO_4^{-2}, Re-Mo, Tc-Mo and Se-Te are described.

RÉSUMÉ

La migration du pertechnétate, du perrhénate, du tellurite, du sélénite et plusieurs autres anions a été examinée avec le butanol, agité avec HCl, HNO_3 ou NH_4OH. Des séparations de Re-Tc, PO_4^{-3}-SO_4^{-2}, Re-Mo, Tc-Mo et Se-Te sont décrites.

ZUSAMMENFASSUNG

Die Wanderung des Pertechnetates, des Perrhenates, des Tellurites, des Selenites und mehrerer anderer Anionen ist untersucht worden mit Butanol, das mit HCl, HNO_3 oder NH_4OH geschüttelt wurde. Separationen von Re-Tc, PO_4^{-3}-SO_4^{-2}, Re-Mo, Tc-Mo und Se-Te werden beschrieben.

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ANION EXCHANGE SEPARATION OF TIN, ANTIMONY AND TELLURIUM

by

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Few references are given in the literature[1,2,3,4] to the ion exchange behavior of tin, antimony and tellurium. Since it was desired to develop radiochemical analysis methods for these elements at this laboratory, data were obtained with oxalate as elutriant which should be of interest, especially in view of the probable complexing[5,6,7] of tin and antimony in this medium.

To determine the degree of resin adsorption, distribution experiments[8] were carried out by shaking for at least 16 hours Dowex-50 (NH_4-form) and Dowex-1 (oxalate form) resins with 0.1*M* oxalic acid solutions (neutralized to different pH's with ammonia) containing ^{113}Sn, ^{124}Sb and ^{125m}Te tracers*. The supernatant liquid was centrifuged and assayed by counting to determine the distribution coefficient, K_d**. As expected, little or no adsorption of tin, antimony or tellurium occurred on Dowex-50. Using Dowex-1, tellurium*** showed no adsorption, tin(IV) varied from K_d of 5800 at pH 1.4 to 6700 at pH 4.2 and the K_d of antimony(V) was 42 at pH 1.4, dropping to 15 at pH of 4.2. No adsorption of the elements occurred at pH 7.4 and 8.8. These results indicated a probable good column separation, though to avoid hydrolysis difficulties, the pH should probably not be above 1.4.

Column experiments were carried out to demonstrate the separation and the elution of the activities was followed by means of a flow pipette, end-window G-M tube, logarithmic-response count rate meter and Brown recorder****. After chlorine oxidation of Sn and Sb tracers, microliter quantities of the tracers in $\sim$ 3*M* HCl were mixed with 0.1*M* oxalic acid and placed on $\sim$ 0.04 cm^2 columns of Dowex-1 (oxalate form) equilibrated with 0.1*M* oxalic acid. Tellurium and antimony(V) were eluted with 0.1*M* oxalate and tin(IV) with 1*M* H_2SO_4*. A typical separation is shown in Fig. 1, with the ^{113m}In daughter of ^{113}Sn eluting above the background level in 0.1*M* oxalate. In fractions containing the activity bands, ^{113}Sn, ^{124}Sb and ^{125m}Te were definitely identified by their characteristic aluminum absorption curves or gamma energies by means of a scintillation spectrometer.

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* The ^{113m}In daughter ($T1/2 = 1.74$ h) of ^{113}Sn was allowed to decay before counting the tin activity.

** $K_d = \dfrac{\text{c/m/g oven dried resin.}}{\text{c/m/ml solution}}$

*** Probably present as Te(IV).

**** A description of the first Manhattan Project work using this type of equipment is given in *J. Am. Chem. Soc.*, 69 (1947) 2769.

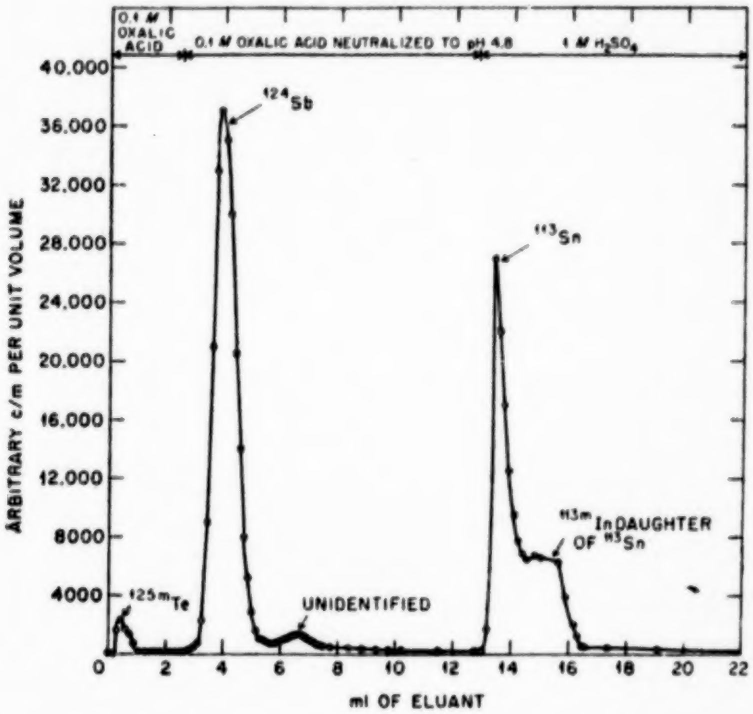

Fig. 1. Separation of tin, antimony and tellurium. 10.5 cm × 0.0384 cm^2 Dowex-^{1} (200-230 mesh) column. 1 void volume = 0.17 ml (∿ 10 min). Flow rate 0.011—0.017 ml/min.

The tracers used, though not carrier-free, loaded** the resin column to only 0.7% in the case of tin and 0.004% with antimony. An attempt to use 5% loading (each) of both tin and antimony resulted in column separation and stopping of the flow, probably due to precipitation and chlorine gas evolution. In the low concentrations used, some of the tin and antimony fractions became cloudy upon standing, even in 0.1*M* oxalic acid or 1*M* sulfuric acid.

It is of further interest to note that antimony requires oxidation to the (V) state to give the above behavior; otherwise, antimony(III), tin(II) and (IV) elute together in 1*M* sulfuric acid. Although columns as long as 30 cm were used, cross contamination to the extent of about 1% was noted for both tin and antimony.

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* Following the suggestion of F. Nelson, ORNL Chemistry Division.

** $\% \text{ Loading} = \frac{\text{Equivalents of ion adsorbed}}{\text{Equivalents of resin used}} \times 100.$

References p. 153.

SUMMARY

Tracer quantities of tin(IV), antimony(V) and tellurium(IV) are separated on Dowex-1 anion exchange resin in 0.1*M* oxalic acid. followed by 1*M* sulfuric acid.

RÉSUMÉ

Des traces d'étain(IV), d'antimoine(V) et de tellure(IV) peuvent être séparées par une résine Dowex-1 (échangeur d'anions) au moyen d'acide oxalique 0.1*M*, puis d'acide sulfurique *M*.

ZUSAMMENFASSUNG

Spuren von Zinn(IV), von Antimon(V) und von Tellur(IV) können getrennt werden mit Hilfe des Harzes Dowex-1 (Anionen-Austauscher) und mittels 0.1*M* Oxalsäure und *M* Schwefelsäure.

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CHROMATOGRAPHIC SEPARATION OF INORGANIC IONS ON SPECIALLY PREPARED CALCIUM SULPHATE STICKS

by

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Successful attempts are being made in this laboratory to effect the separation of inorganic ions using a simplified chromatographic technique. For this purpose newer adsorbents have been sought for with some success. This idea originated with asbestos chromatography, in which slices of asbestos millboard cut longitudinally could be used for the separation of certain cations. By this technique, qualitative separations of Cu^{+2} — Cd^{+2}, $As^{+3}Sb^{+3}$ — Sn^{+2} [1], Hg^{+} — Pb^{+2}, Hg^{+2} — Pb^{+2}, Hg^{+2} — Cu^{+2}, Pb^{+2} — Cu^{+2} [2], Cu^{+2} — Fe^{+3}, Mn^{+2} — Zn^{+2}, Fe^{+3} — Zn^{+2} and Co^{+2} — Ni^{+2} [3], have been effected. Bleached cane has been successfully used to effect separation of Cu^{+2} — Cd^{+2}, As^{+3} — Sb^{+3} — Sn^{+2}, Cu^{+2} — Pb^{+2}, Hg^{+2} — Cu^{+2} [4].

Defibrised jute plant sticks have been found useful in the separation of inorganic ions and the successful separation of Hg^{+} — Pb^{+2}, Hg^{+2} — Pb^{+2}, Hg^{+2} — Cu^{+2}, Cu^{+2} — Cd^{+2}, As^{+3} — Sb^{+3} — Sn^{+2}, Cu^{+2} — Fe^{+3} has been effected[5]. Calcium sulphate in the form of specially prepared sticks has been found to be of much promise in effecting the separation much more quickly, identification being completed in less than 10 minutes, and the successful separation of Cu^{+2} — Cd^{+2}, As^{+3} — Sb^{+3} — Sn^{+2} have been reported[6].

This paper records the application of the method to the successful qualitative separation of nearly a dozen cation pairs and in all cases the method was pronouncedly more rapid.

The calcium sulphate sticks have the advantage that the separation is completed quickly in about less than 10 minutes, which in consideration of the normal character of chromatographic separation may be looked upon as insignificant. The method therefore claims to be a rapid method of chromatographic analysis. There is also the advantage that the portions containing the respective bands can be cut out and treated suitably for further confirmation.

PREPARATION OF STICKS

The calcium sulphate was made in the form of round sticks of about 6-8 inches length and 6-8 mm diameter. In the preparation of the sticks, calcium sulphate ($CaSO_4,2H_2O$, precipitated) was mixed intimately with Plaster of Paris in the proportion of 55 ($CaSO_4,2H_2O$): 45 (Plaster of Paris), moistened with water, kneaded and shaped in the form of sticks in thick paper moulds. The sticks were then allowed to dry slowly in a warm chamber at a temperature just 5° C above normal temperature for about 4 hours. The paper wrappers were next carefully taken out and the sticks were placed in dry air in a large closed space for about a week, avoiding all chances of contamination with dust particles.

THE TECHNIQUE

To carry out the analysis, a drop or two of the test solutions was put on the sticks which were then introduced into test tubes containing 3-4 ml of water acidified with dilute hydrochloric acid in most cases, with which the spot of the test solution is to be irrigated. The sticks were kept vertical by means of bored corks fitting the tubes. The spot is kept 1″-1½″ above the surface of the irrigant in the tubes. Water gradually rose and reached the 'spot' and was allowed to rise further till it rose well beyond the 'spot' and there was no further appreciable rise. While still moist, the sticks were held in a stream of well-washed hydrogen sulphide gas, which was used for identification in most cases; in case of identification by liquid reagents, the sticks were allowed to dry and then sprayed with the reagent.

RESULTS

Cu^{+2} — Sb^{+3}. Two clearly separated bands were obtained. The upper band was orange and the lower one, above the 'spot', was black. The two bands were almost as broad as each other.

Bi^{+3} — Sb^{+3}. Two clearly defined bands were obtained, one orange and the other brown, above the orange. The orange one was comparatively broad.

Cd^{+2} — Sb^{+3}. Two bands clearly separated developed, one yellow and the other brown, the yellow above the brown. Both bands were equally broad.

Cd^{+2} — Sn^{+2}. A bi-coloured chromatogram was obtained consisting of a brown and a yellow band. The yellow band was broader than the brown and was formed above the latter.

Hg^{+2} — As^{+3}. Two bands were obtained. The upper band was yellow and the lower black. The yellow band was broader and at a considerably large distance from the black.

Hg^{+2} — Sb^{+3}. Two well-developed and clearly defined bands were obtained. The lower band was orange and was broader than the upper band which was black. There was a considerable distance between the two.

Cu^{+2} — As^{+3}. Two clearly separated well-developed bands were obtained, one yellow and the other black, yellow above the black. The yellow band was broader than the black.

Bi^{+3} — As^{+3}. Two clearly defined bands were obtained, the one brown and the other yellow. The yellow band was broader than the brown and was formed above the latter.

Hg^{+2} — Cu^{+2}. The 'spot' of the test solution was irrigated with water alone, 3-4 ml of which were placed in the test tube. After irrigation, the stick was sprayed with a solution of potassium ferrocyanide reagent. Immediately a broad red coloured band appeared and then the stick was held in bright sunlight when a blue coloured band, a little less broad, but distinctly developed, was formed above the red band. The white mercury ferrocyanide changed almost immediately in light to a blue colour.

Cu^{+2} — Fe^{+3}. The irrigant was water alone as in the previous experiment. The stick was then sprayed with a solution of potassium ferrocyanide reagent. Two distinctly developed broad bands were obtained, chocolate red and blue. The blue band was above the chocolate.

SUMMARY

It has been shown[6] that specially prepared calcium sulphate sticks are suitable as adsorbent bodies in the chromatographic separation of inorganic ions. With the help of these sticks separations of Cu^{+2} — Sb^{+3}, Bi^{+3} — Sb^{+3}, Cd^{+2} — Sb^{+3}, Cd^{+2} — Sn^{+2}, Hg^{+2} — As^{+3}, Hg^{+2} — Sb^{+3}, Cu^{+2} — As^{+3}, Bi^{+3} — As^{+3}, Hg^{+2} — Cu^{+2}, Cu^{+2} — Fe^{+3} have been effected.

RÉSUMÉ

Il est démontré[6] que des baguettes de sulfate de calcium, spécialement préparées, peuvent servir d'absorbants pour la séparation chromatographique des ions inorganiques. Les séparations suivantes ont pu être effectuées: Cu^{+2} — Sb^{+3}; Bi^{+3} — Sb^{+3}; Cd^{+2} — Sb^{+3}; Cd^{+2} — Sn^{+2}; Hg^{+2} — As^{+3}; Hg^{+2} — Sb^{+3}; Cu^{+2} — As^{+3}; Bi^{+3} — As^{+3}; Hg^{+2} — Cu^{+2}; Cu^{+2} — Fe^{+3}.

References p. 157.

ZUSAMMENFASSUNG

Es wird gezeigt[6], dass speziell präparierte Stäbchen aus Calciumsulfat als Absorptionsmittel verwendet werden können für die chromatographische Trennung anorganischer Ionen. Die folgenden Abtrennungen konnten auf diese Weise durchgeführt werden: Cu^{+2} — Sb^{+3}; Bi^{+3} — Sb^{+3}; Cd^{+2} — Sb^{+3}; Cd^{+2} — Sn^{+2}; Hg^{+2} — As^{+3}; Hg^{+2} — Sb^{+3}; Cu^{+2} — As^{+3}; Bi^{+3} — As^{+3}; Hg^{+2} — Cu^{+2} —; Cu^{+2} — Fe^{+3}.

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SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF SELENIUM WITH DIAMINOBENZIDINE

by

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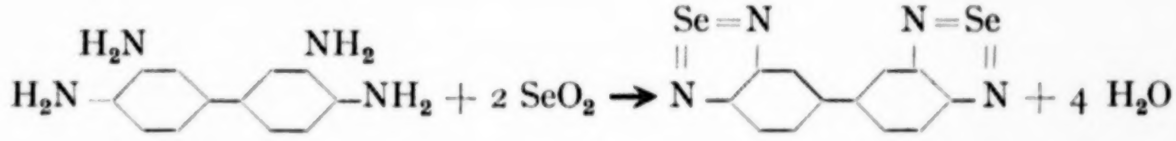
INTRODUCTION

Some years ago one of us* proposed diaminobenzidine as a sensitive specific reagent for the qualitative determination of selenium. This reagent forms with selenous acid an intense yellow piazselenol:



Absorption spectrum of the piazselenol

To determine the characteristic absorption curve of the piazselenol we have measured the extinction of a solution of the compound in the region 330-450 mμ. Previous gravimetric experiments had shown that the formation of the selenol is quantitative, although coprecipitation or adsorption of the reagent itself could not be avoided, causing too high results in the gravimetric procedure.

The selenol formation was carried out in an acidic medium, as the reagent itself, diaminobenzidine tetrachloride, is rapidly oxidized by the air in neutral or alkaline solutions. Furthermore the selenol is soluble, to only a small extent, in acidic solutions.

Procedure. Solutions used:

1) Stock solution of selenous acid: 0.982 mg Se/ml in HCl.
2) 0.1% diaminobenzidine tetrachloride in HCl.
3) Standardized HCl.

In a graduated flask of 50 ml one introduces 25 ml of a solution containing approximately 5 μg Se (as SeO_2) and 25 ml 0.1% diaminobenzidine. The solutions contained the appropriate amounts HCl (see Table I). Measurements were carried out with a Beckman DU spectrophotometer using a tungsten lamp, the violet filter below 350 mμ and 1 cm Corex cells. The sensitivity of the instrument was kept constant at 3 turns from its clockwise limit. A blank containing no selenium was used in all these experiments. The results obtained are summarized in Table I.

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* J. HOSTE, *Anal. Chim. Acta*, 2 (1948) 402.

TABLE I

N HCl	Wave length of maximum extinction	Extinction	Time for quantitative formation
0.08	347—349 mμ	0.444	50 minutes
0.100	347—349 mμ	0.455	50 minutes
0.120	347—349 mμ	0.463	50 minutes
0.500	346—347 mμ	0.490	1 h 10 min
1.00	345—346 mμ	0.550	3 h 15 min
2.00	347—348 mμ	0.550	3 h 25 min
3.00	348—349 mμ	0.577	3 h 25 min

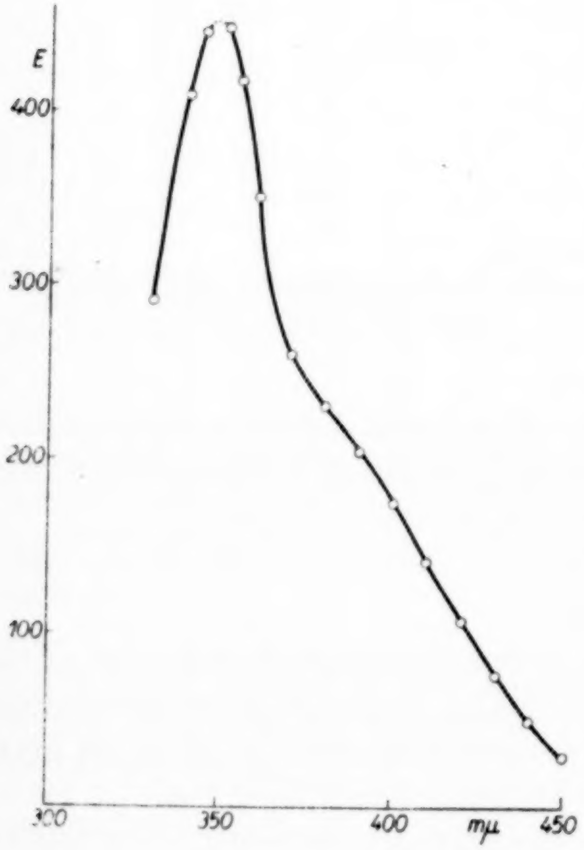

Fig. 1

The experiments show that the extinction increases with increasing acidity. The quantitative formation of the selenol is, however, strongly delayed with increasing acidity so that it was necessary to make a compromise between sensitivity and reaction speed.

The further study of the reaction was therefore carried out in 0.1*N* HCl at 348 mμ using Corex cells and the built-in violet filter. Fig. 1 represents the absorption curve of the selenol in 0.1*N* HCl in the region 330—450 mμ.

Molecular extinction coefficient:

$$\varepsilon = \frac{E \cdot d}{C} = \frac{0.455}{4.46 \cdot 10^{-6}} = 10{,}200$$

Validity of Lambert-Beer-law

The law of LAMBERT-BEER is valid between 0.25 and 2.5 μg Se per ml. At higher Se concentrations the selenol precipitates, causing erratic results. Therefore solutions having an extinction higher than $E = 0.690$ should not be used.

Table II gives the data for a calibration curve obtained by the procedure described above.

TABLE II

μg Se/ml	E	k	Δk
0.25	0.046	184	1.6
0.50	0.092	184	1.6
0.75	0.137	183	0.6
1.00	0.183	183	0.6
1.25	0.229	183	0.6
1.50	0.271	181	1.4
1.75	0.317	181	1.4
2.00	0.368	184	1.6
2.25	0.407	181	1.4
2.50	0.450	180	2.4

$$\text{Mean extinction coefficient: } \frac{\Sigma k}{10} = 182.4$$

$$\text{Mean error } \frac{\Sigma \Delta k}{10} = 1.3 \text{ or } 0.72\%$$

Influence of excess reagent

Reagent concentrations from 0.1 up to 0.4% do not influence the extinction.

Stability of the color

The color is stable for at least 5 hours. The blank colors slowly, due to oxidation by the air, and must be prepared simultaneously with the unknown and stored under the same conditions.

Influence of foreign ions

The influence of foreign anions and cations was investigated. The salts of the cations were present either as chlorides or as nitrates, of the anions as their sodium or potassium salts. All ions were present in concentrations 100 times as great as that of the selenium. Results are summarized in Table III.

One can conclude that the majority of the most common ions, even in quantities 100 times as great as that of the selenium, do not interfere, except by their own color as in the case of Cr. TeO_2 does not react, whereas SO_2 disturbs the reaction by giving a colorless precipitate. The sulfate, however, does not disturb the spectrophotometric determination. Fe(III) disturbs but can be effectively masked by adding 10 ml of a 1.5% NH_4F solution. Copper causes too high results and should be masked by adding 10 ml of a 2% ammonium oxalate solution.

TABLE III

Foreign ion	Extinction	% error
Bromide	0.458	+ 0.76%
Chloride	0.453	— 0.44
Nitrate	0.468	+ 2.8
Phosphate	0.444	— 2.4
Sulfate	0.460	+ 1.1
Citrate	0.467	+ 2.6
Oxalate	0.455	0.0
Tartrate	0.468	+ 2.8
Al	0.461	+ 1.3
Ba	0.454	— 0.2
Ca	0.454	— 0.2
Cd	0.463	+ 1.7
Cr	0.558	+ 23
Co	0.461	+ 1.3
K	0.455	0.0
Mg	0.451	— 0.9
Mn	0.463	+ 1.7
Mo (VI)	0.473	+ 3.9
Ni	0.467	+ 2.9
Te (IV)	0.453	— 0.4
Na	0.450	— 1.1
NH_4	0.458	+ 0.7
Zn	0.460	+ 1.1

ACKNOWLEDGEMENT

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SUMMARY

Diaminobenzidine is suitable for the spectrophotometric determination of traces of selenium. The reaction is very sensitive, the molecular extinction coefficient being as high as 10,200. The reaction is specific, the most common ions causing no perturbation. The procedure is especially valuable for the determination of traces selenium in tellurium and in sulfur, provided that the latter is present in the sulfate form.

RÉSUMÉ

La diaminobenzidine convient au dosage spectrophotométrique des traces de sélénium. La réaction est très sensible, le coefficient d'extinction moléculaire étant 10,200; elle est également spécifique, les éléments les plus courants ne gênent pas. Ce procédé est particulièrement avantageux pour le dosage de traces de sélénium dans le tellure et dans le soufre, à condition que ce dernier se trouve sous forme de sulfate.

ZUSAMMENFASSUNG

Das Diaminobenzidin eignet sich für die spektrophotometrische Bestimmung von Selenium in Spuren. Die Reaktion ist sehr empfindlich, der molare Extinktionskoeffizient ist 10,200. Die Reaktion ist zudem spezifisch; die geläufigsten Elemente stören nicht. Dieses Verfahren ist speziell vorteilhaft für die Bestimmung von Selen-Spuren im Tellur und im Schwefel, unter der Bedingung, dass dieser letzte in der Form von Sulfat vorliegt.

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THE COLORIMETRIC DETERMINATION OF SILICATE WITH SPECIAL REFERENCE TO SEA AND NATURAL WATERS

by

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Silicon occurs in the sea in small amounts (0.02-4.0 mg Si/l)[1] principally as silicate, but perhaps also as colloidal silica. A knowledge of its concentration and distribution is useful to both the marine biologist and the oceanographer[2]. In early work[3,4] silicon was determined gravimetrically, but this method is both time-consuming and inaccurate at the concentrations of silicon encountered in sea-water. JOLLES AND NEURATH[5] suggested a colorimetric method for the determination of silicon based on the formation of yellow silicomolybdic acid. This method was applied to the analysis of natural waters by DIENERT AND WANDENBULCKE[6]; subsequent developments of this method have been reviewed by SCHWARTZ[7], and by LACROIX AND LABALADE[8]. ATKINS[9] applied the method to the analysis of sea-water, and his procedure has been used with minor modifications by several other workers[10-19]. The yellow silicomolybdate method when used for the analysis of sea-water suffers from several disadvantages.

1) The colour is only stable for about 5 minutes and thereafter fades fairly rapidly. This fading has been attributed by STRICKLAND[20] to the conversion of the primarily formed β-silicomolybdic acid to the less strongly absorbing isomeric α-silicomolybdic acid.

2) The absorption maximum of the silicomolybdic acid is overlapped by that of the excess molybdate reagent used in its formation, and hence absorption measurements must be made in a region where the absorption is changing rapidly with wavelength.

3) The sensitivity is inadequate for the determination of low silicon concentrations (below 0.1 mg/l).

4) At higher concentrations BEER's law is not obeyed[8].

ISAACS[21] first observed that silicomolybdic acid could be selectively reduced, in the presence of excess molybdate, to molybdenum blue. Since this time, many

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reductants have been employed for the reduction of silicomolybdic acid to molybdenum blue, *viz.*, stannous chloride[22-26], sodium sulphite[27-29], ferrous sulphate[30], 1-amino-2-naphthol-4-sulphonic acid[29, 31-37] and hydroquinone[29, 38-41].

Only stannous chloride[22] appears to have been used in the determination of silicon in sea-water. A drawback to this method is the instability of the molybdenum blue colour, which fades rapidly. Experiments were therefore made to compare the effectiveness of a number of organic reducing agents for the reduction of silicomolybdic acid to molybdenum blue. The results, shown in Table I, were obtained using the reducing agents under conditions (which were found individually for each reagent) producing the greatest absorption.

TABLE I

COMPARISON OF REDUCING AGENTS FOR REDUCTION OF SILICOMOLYBDIC ACID TO MOLYBDENUM BLUE

Reducing agent	I	II	III	IV	V
Redox potential (V vs S.C.E.)	—0.389	—0.308[42]	—0.357[42]	—0.434[42]	—
Wavelength max. abs. (mμ)	810	812	810	810	825
Optical density*	0.521	0.500	0.502	0.495	0.456
Time max. colour development					
distilled water	15 min	2 h	2 h	30 min	10 min
sea water	10 min	60 min	—	—	—
% fall off colour/hour					
distilled water	1.0	**	***	***	†
sea water	4.4	***	—	—	—

* For 4 μg silicon in 50 ml measured in 7.62 cm cell, reagent blank deducted.
** Constant 24 h with 4 μ g Si, 72 h 30 μg Si.
*** Constant 24 h.
† Constant 72 h with 200 μg Si with slight precipitation after 24 h.

In all cases silicomolybdic acid was formed by treating 20 ml of the solution containing the silicate-silicon with 3.0 ml of 2.0% ammonium molybdate, 0.6*N* with respect to hydrochloric acid. After 10 minutes 5 ml of 50% v/v sulphuric acid were added, followed after 5 minutes by the reductant:

I. Stannous chloride. 1.00 ml of 0.15*N* hydrochloric acid containing 0.25% of stannous tin.

II. *p*-Methylaminophenol sulphate (metol). 5.0 ml of a solution containing 2.0% of metol and 1.2% of anhydrous sodium sulphite.

III. *p*-Dihydroxybenzene (hydroquinone). 5.0 ml of a solution containing 4.0% of hydroquinone and 1.2% of anhydrous sodium sulphite.

IV. 2.4-Diaminophenol hydrochloride (amidol) 4.0 ml of a solution containing 2.0% of amidol and 3.0% of anhydrous sodium sulphite.

V. 1-Amino-2-naphthol-4-sulphonic acid. 5.0 ml of a solution containing 0.15% of 1-amino-2-naphthol-4-sulphonic acid, 9.0% of sodium bisulphite, and 0.7% of anhydrous sodium sulphite.

Thus, although stannous chloride gives a slightly greater sensitivity than the other reductants, the colour fades rather rapidly owing to the more rapid oxidation of stannous chloride in sea water; this detracts from its usefulness when large numbers of determinations have to be made. Of the other reductants tested, neither hydroquinone nor amidol yielded stable reagent solutions, and they became partly oxidized to yellow and brown products respectively during the determination. Although the maximum colour intensity was rapidly attained with 1-amino-2-naphthol-4-sulphonic acid reagent, the sensitivity was lower, and the reagent blank high; furthermore, the determinations tended, on standing, to throw down a colourless precipitate. Metol was finally selected as the most suitable reducing agent on the grounds of cost, accuracy, and of the high stability of both the reagent and the final colour.

The wavelength of maximum absorption of the reduced silicomolybdic acid is practically independent of the reducing agent used, which suggests that the reduced product is not colloidal in nature. On the other hand, the shape of the absorption curve and the wavelength of maximum absorption of the molybdenum blue derived from phosphomolybdic acid is dependent upon the reducing agent, owing to the variation in particle size distribution of the colloidal particles produced by different reductants.

It should be noted that the absorption maximum of the reduced silicomolybdate is in the near infra red, hence maximum sensitivity for silicon will not be attained using colorimeters equipped with barrier layer photoelectric cells having a low sensitivity in this spectral region.

The investigation of the optimum conditions for the determination of silicon has been carried out in two parts, firstly the formation of silicomolybdic acid and secondly its reduction.

Conditions for formation of silicomolybdic acid

The formation of silicomolybdic acid in solution is governed primarily by the hydrogen ion concentration and by the concentration and nature of both the molybdate and silicic acid species present.

Although there is considerable controversy about the exact nature of the molybdate species existing in solution at particular acidities, there seems to be general agreement that in the pH range 6.5-14, the normal molybdate ion $[MoO_4]^{-2}$ predominates. At higher acidities polymerisation sets in, the degree of polymerisation increasing rapidly with the acidity of the solution. LINDQVIST[43] considers the reactions on acidification to be

$$[MoO_4]^{-2} \rightarrow [Mo_7O_{24}]^{-6} \rightarrow [Mo_8O_{26}]^{-4} \rightarrow \text{larger complexes.}$$

The rate of formation of silicomolybdate is therefore likely to be greatly dependent upon the degree of polymerisation of the molybdate from which it is formed.

Silicic acid also undergoes polymerisation in acidic solution. Thus WEITZ *et al.*[44] showed that in dilute solution (50-60 p.p.m. SiO_2) the formation of silicomolybdic acid is complete in 75 sec from orthosilicate, in 10 minutes from disilicic acid and in 1 hour for higher condensed acids. High molecular weight polysilicic acids did not react at all under their conditions. CHOW AND ROBINSON[45], who examined a series of mixtures having various $Na_2O : SiO_2$ ratios, found that complete formation of silicomolybdic acid was only attained if the $SiO_2 : Na_2O$ ratio was less than 1.

Thus the main controlling factor in the formation of silicomolybdic acid appears to be the acidity of the solution. To determine the optimum acidity for the formation of silicomolybdic acid, samples of sodium silicate solution containing 40 μg of silicon were treated with various volumes of 1*N* hydrochloric acid, diluted to 40 ml, 5 ml of 5% ammonium molybdate solution added, and the solution diluted to 50 ml. The intensity of the yellow colour was measured at 404 mμ (0.03 mm slit) in 7.62 cm cells. The results, which are shown in Table II, indicate that the formation of silicomolybdic acid is complete over the pH range 0.64-1.45, but that the rate of formation is much reduced in solutions more acidic than pH 1.0, presumably owing to polymerisation of the silicic acid. With less than 4 ml of 1*N* acid, the acid : molybdate ratio lies within the range for the formation of some α-silicomolybdic acid and explains the lack of concordance in the values obtained. In all further work a volume of 4 ml of 1*N* hydrochloric acid was employed.

The effect of variation of the ammonium molybdate concentration at this acidity was next investigated. It was found (Table III) that although the ammonium molybdate concentration made little difference to either the final colour intensity, or the pH of the solution, it exerted a very marked effect on the rate of silicomolybdic acid formation. The optimum colour formation occurred with 3 ml of 5% ammonium molybdate solution, and this amount was used in all subsequent work. Larger volumes of molybdate solution tended to increase the blank excessively.

The optimum conditions found for the formation of the silicomolybdic acid are similar to those used by ARMSTRONG[22] in his method for the determination of silicon in sea-water, and lie in the range for the formation of β-silicomolybdic acid found by STRICKLAND[20].

TABLE II

EFFECT OF ACID CONCENTRATION ON FORMATION OF SILICOMOLYBDIC ACID

40 μg Si + x ml of 1N HCl diluted to 40 ml, 5 ml 5% ammonium molybdate added and the solution was diluted to 50 ml and measured at 404 mμ (0.03 mm slit) in 7.62 cm cells

x ml of 1N HCl	Time of development (min)	Maximum optical density Blank	Solution*	pH
0.5	6	0.004	0.280	3.40
1.0	3	0.014	0.415	2.20
1.5	3	0.024	0.417	1.94
2.0	4	0.025	0.422	1.76
3.0	4	0.029	0.419	1.45
4.0	8	0.029	0.426	1.28
5.0	7	0.030	0.428	1.16
6.0	10	0.032	0.429	1.07
7.0	8	0.032	0.427	1.02
8.0	12	0.032	0.426	0.96
9.0	15	0.035	0.422	0.91
10.0	22	0.037	0.420	0.87
12.0	30	0.036	0.420	0.80
15.0	200	0.039	0.419	0.72
20.0	>6 h.	0.033	0.419**	0.64

* Less blank.
** After 20 hours.

TABLE III

EFFECT OF AMMONIUM MOLYBDATE CONCENTRATION ON FORMATION OF SILICOMOLYBDIC ACID

20 ml silicate solution (40 μg Si) + 4 ml N HCl + x ml of y % ammonium molybdate solution, diluted to 50 ml and measured at 404 mμ (0.03 mm slit) in 7.62 cm cells

Ammonium Molybdate		Time for maximum colour (min)	Optical Density after 10 minutes Blank	Solution*	Maximum Solution*	pH
x ml	y %					
5	0.25	—	0.000	0.000	—	1.15
10	0.25	⩾ 240	0.003	0.020	0.321**	1.17
15	0.25	> 200	0.003	0.134	0.407***	1.18
5	1.00	40	0.012	0.313	0.416	1.20
10	1.00	8	0.013	0.422	0.422	1.20
15	1.00	6	0.019	0.426	0.426	1.22
20	1.00	6	0.025	0.427	0.427	1.26
5	5.00	6	0.029	0.428	0.428	1.27
10	5.00	6	0.058	0.430	0.430	1.38
15	5.00	< 2	0.084	0.427	0.427	1.56

* Less reagent blank.
** After 234 minutes.
*** After 200 minutes.

Stability of silicomolybdic acid in highly acidic media

In order to avoid the reduction of the excess molybdate reagent it is essential for the reduction of silicomolybdic acid to be carried out in highly acidic solution (at least $1.5N$ with respect to sulphuric acid). The stability of silicomolybdic acid in the presence of sufficient acid to prevent the reduction of ammonium molybdate has been investigated. Samples (20 ml) of a solution containing 200 µg Si/l were treated with 3 ml of acid-molybdate reagent. After standing 10 minutes to complete the formation of silicomolybdic acid, 5 ml of 50% v/v sulphuric acid was added. After various periods the solutions were treated with 5 ml of sulphite-metol reagent (2% and 1.2% in metol and sodium sulphite respectively), and diluted to 50 ml. The optical densities of the solutions were measured at 812 mµ after 3 hours. Similar experiments were performed with 40 ml samples of the same silicate solution using ARMSTRONG's[22] method but allowing various periods to elapse between the acidification with 50% sulphuric acid and the addition of stannous chloride reductant. In each case it was found that the optical density of the solution decreased roughly linearly with the time elapsing between acidification and addition of reducing agent. The decrease per minute was 1.0% with metol and 0.43% with stannous chloride. The difference may be attributed to the different final normality of acid used in the two methods. It is therefore preferable, both for accuracy and simplicity, to add the acid and reductant together rather than separately.

Conditions for the reduction of silicomolybdic acid with metol

In order to determine the most sensitive conditions for the reduction of silicomolybdic acid, the effect on the colour production of variation of the amounts of sulphuric acid- sodium sulphite and metol added was examined. In each case samples of 20 ml of silicate solution containing 200 µg Si/l were treated with 3 ml of the acid-molybdate reagent (see below). After 10 minutes a mixture of the appropriate amounts of the reagents was added and the solution made up to 50 ml. The optical density was measured at 812 mµ in a 7.62 cm cell after 3 hours. Blank determinations were run in a similar fashion on distilled water.

Variation of sulphuric acid concentration

The reducing agent consisted of 5 ml of a solution 1.20% with respect to sodium sulphite and 2.0% with respect to metol, together with varied amounts of 50% v/v sulphuric acid.

The results, Table IV, show that to prevent the reduction of the excess molybdate at least 2 ml of 50% sulphuric acid should be present; a five fold excess of acid produces no further effect on either the blank or the determination.

TABLE IV

OPTICAL DENSITIES OF SOLUTIONS REDUCED IN THE PRESENCE OF VARIOUS AMOUNTS OF 50% SULPHURIC ACID.

ml of 50% sulphuric acid	0	0.25	0.5	1.0	2.0	3.0	4.0	5.0	7.0	9.0
4 µg Si	2.390	0.930	0.542	0.531	0.534	0.523	0.523	0.522	0.522	0.524
Blank	1.560	0.415	0.054	0.043	0.026	0.024	0.020	0.023	0.022	0.025
Difference	0.830	0.515	0.488	0.488	0.498	0.499	0.503	0.499	0.500	0.499

Variation of metol concentration

Silicomolybdic acid formed from 4 µg silicon was reduced with a mixture of 2 ml of 3% sodium sulphite, 5 ml of 50% sulphuric acid and varied amounts of 2% metol solution. The results, which are shown in Table V, indicate that for complete reduction in 3 hours, at least 4 ml of metol solution are required, but that the same value is obtained with only 0.5 ml if a reduction period of 12 hours is used.

TABLE V

OPTICAL DENSITIES OF SILICOMOLYBDIC ACID SOLUTION (4 µg Si) REDUCED WITH A REDUCTANT CONTAINING VARIOUS VOLUMES OF 2% METOL SOLUTION FOR 3 AND 12 HOURS

ml of 2% metol	0	0.5	1.0	2.0	4.0	5.0	6.0	8.0	10.0	12.0
3 hours reduction*	0.006	0.479	0.489	0.495	0.499	0.500	0.501	0.505	0.504	0.502
12 hours reduction*	0.010	0.499	0.499	0.498	0.500	0.501	0.501	0.505	0.503	0.504

* After deduction of reagent blank.

Variation of sulphite concentration

A reducing agent composed of a mixture of 4 ml of 2% metol, 5 ml of 50% sulphuric acid and various amounts of 3% sodium sulphite was used for the reduction of silicomolybdic acid. The optical densities of the solutions were measured after 3 hours and 18 hours. It will be seen (Table VI) that the presence of sulphite is essential for the rapid and efficient reduction of silicomolybdic acid by metol. For reductions to be complete within 3 hours the reductant must contain at least 1 ml of 3% sodium sulphite.

On the basis of these experiments it was decided to employ as reducing agent a mixture containing 2 ml of 3% sodium sulphite, 5 ml of 2% metol, and 6 ml

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TABLE VI

OPTICAL DENSITIES OF SOLUTIONS CONTAINING 4 μg SILICON AFTER REDUCTION WITH METOL REDUCTANT CONTAINING VARIOUS VOLUMES OF 3% SODIUM SULPHITE

ml of 3% Na_2SO_3	0.0	0.1	0.2	0.4	0.6	0.8	1.0	2.0	4.0	6.0
3 hours reduction*	0.103	0.428	0.461	0.477	0.481	0.489	0.498	0.502	0.500	0.502
18 hours reduction*	0.268	0.458	0.481	0.497	0.501	0.498	0.499	0.501	0.500	0.502

* After deduction of reagent blank.

of 25% sulphuric acid for each determination. Oxalic acid (3 ml of 10%) was also incorporated in the reagent in order to suppress interference due to phosphate (see below).

Using the acid-molybdate reagent, followed after various intervals by the above reductant, it was found that the formation of silicomolybdic acid was complete in approximately 7 minutes in distilled water and that the complex remained stable for at least an hour. The reduction of silicomolybdic acid to molybdenum blue was complete at room temperature (20°) in 90 minutes with 4 μg of silicon and in 150 minutes with 30 μg of silicon, the colour was stable for at least 48 hours.

Method

All measurements of optical density were made with a Unicam S.P.500 spectrophotometer. pH measurements were made by means of a Cambridge Instrument's pH meter using a glass electrode.

Reagents

All reagents and solutions must be made up with freshly distilled water.

1. *Acid ammonium molybdate.* Shake 2 g of ammonium molybdate with *ca.* 70 ml of water, add 6 ml of concentrated hydrochloric acid to complete the solution of the salt. Dilute to 100 ml and, if necessary, filter through an ashless filter paper. Since the reagent takes up silicon from glass it should be stored in polythene bottles.

2. *Oxalic acid.* Dissolve 10 g of oxalic acid dihydrate in water, dilute to 100 ml, and filter.

3. *Sulphuric acid.* 25% v/v.

4. *Metol-sulphite solution.* Dissolve by shaking, 5 g of metol in *ca.* 240 ml of water, containing 3 g of anhydrous sodium sulphite, and dilute to 250 ml. The solution, after filtration through a Whatman No. 1 filter paper, should be stored in a dark glass bottle.

Reducing agent

Mix 100 ml of the metol-sulphite solution with 60 ml of 10% oxalic acid and add, whilst cooling, 120 ml of 25% sulphuric acid, dilute to 300 ml. The fresh reducing agent should be prepared fortnightly.

5. *Standard sodium silicate solution.* Prepare from commercial sodium silicate solution, standardized gravimetrically according to WASHINGTON[46], a solution containing 10 mg of silicate-silicon per litre. Suitable dilutions from this stock solution are used for calibration.

Treatment of apparatus

Graduated flasks should be allowed to stand overnight with a mixture of concentrated nitric and sulphuric acids (1: 1) to render them insoluble. After this treatment they should be well washed with tap water and distilled water. The flasks may be drained, but should not be allowed to become completely dry as this appears to render them more soluble.

Method

Pipette 20 ml of the sample* (up to 60 μg Si) into a 50 ml graduated flask containing 3 ml of the acid molybdate reagent and mix thoroughly. After 10 minutes add 15 ml of the reducing agent from a tilt measure, and make up to 50 ml with distilled water, allow to stand for 3 hours. Measure the optical density of the solution at 812 mμ against distilled water in the compensating cell. Run a blank determination using distilled water and calibrate the method with known amounts of silicate solution. The calibration remains constant for many months; 4 μg of silicate-silicon give an optical density in a 7.62 cm (3 inch) cell of 0.500 after deduction of the reagent blank (usually 0.010).

Beer's Law and reproducibility

Various amounts of silicate (0.05-60.0 μg Si) in 20 ml of distilled water were examined according to the procedure described in the experimental section, the optical densities being measured at 812 mμ in cells of the appropriate length. The results, (Table VII) show a high degree of reproducibility and close adherence to Beer's Law, up to a concentration of at least 3 p.p.m.

Interference of foreign ions

The interference of several salts on the determination of silicon by the proposed method was evaluated by adding to 20 ml of the solution of the salt in question, 1 ml of a solution containing 4 mg of silicate-silicon/l. After development of the

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* Take 15 ml of sea-water and add *ca.* 5 ml of distilled water (see p. 175).

TABLE VII

Si (μg)	No. of determinations	Mean optical density* (1 cm cell)	Standard deviation %	Deviation from linearity (%)
0.05	5	0.00082**	4.38	+0.06
0.10	5	0.00165**	2.18	+0.43
0.20	5	0.00321**	0.81	—2.26
0.50	5	0.00824**	0.44	+0.43
1.00	5	0.01630**	0.88	—0.67
1.50	5	0.02451**	0.00	—0.43
2.00	5	0.03270***	0.21	—0.37
3.00	5	0.04925***	0.28	+0.06
4.00	5	0.06576***	0.25	+0.18
5.00	5	0.08250***	0.13	+0.55
6.00	5	0.09810***	0.57	—0.37
8.00	5	0.1313	0.75	0.00
10.00	5	0.1643	0.68	+0.12
15.00	5	0.2458	0.55	—0.12
20.00	5	0.3290	0.63	+0.24
30.00	5	0.4932	0.26	+0.18
45.00	5	0.7380	0.38	—0.06
60.00	5	0.9816	0.22	—0.31

* Less blank.
** Measured in 15.24 cm cell.
*** Measured in 7.62 cm cell.

Note: Amount of silicon in μg $= \dfrac{\text{Optical density}}{0.01641}$

colour, the solutions were measured at 812 mμ in 7.62 cm cells. Similar runs were carried out using 20 ml of the salt solution, without the addition of silicon. 4 μg of silicate-silicon gave an optical density of 0.500 (less blank), with a reagent blank of 0.010. The results are shown in Tables VIII and IX.

The interference of copper, ferrous iron, cobalt, and nickel is due to the absorption of their ions at 812 mμ. Copper at a concentration of less than 10 p.p.m. (Cu:Si = 50:1) causes negligible error. At higher concentrations (up to 100 p.p.m.) the interference of copper is additive and may be compensated for by deducting the absorption at 812 mμ of 20 ml of the original solution diluted to 50 ml.

Ferric iron interferes with the determination of silicon owing to the precipitation of reddish-brown ferric molybdate during the formation of the silicomolybdic acid. This precipitation may be prevented by making the test solution 0.1*N* with sulphuric acid and permits the determination of silicon in the presence of 30 p.p.m. of ferric iron with a 5% error. The error can be much diminished by reducing the iron to the ferrous state with a solution of hydroxylamine hydrochloride (1 ml of 10% $NH_2OH.HCl$) prior to the formation of the silicomolybdic acid. In this way 0.2 p.p.m. of silicon can be determined in the presence of up to 100 p.p.m. of ferric iron with an error of less than 1%.

TABLE VIII

INTERFERENCE OF FOREIGN CATIONS ON DETERMINATION OF 4 µg SILICON

Cation	Added as	Concentration of element p.p.m.	Optical density 4 µg Si	Blank	Difference
Aluminium	$Al.NH_4(SO_4)_2.12H_2O$	250	0.511	0.010	0.501
Ammonium	NH_4Cl	500	0.512	0.015	0.497
Antimony	$SbBr_3$	500	0.515	0.024	0.491
Barium	$BaCl_2.2H_2O$	500	0.507[a]	0.010[a]	0.497
Beryllium	$Be(NO_3)_2.5H_2O$	500	0.527	0.049	0.478
Bismuth	$Bi(NO_3)_3.3H_2O$	500	0.512	0.012	0.500
Cadmium	$CdCl_2.2\frac{1}{2}H_2O$	500	0.499	0.019	0.480
Caesium	$CsCl$	500	0.506	0.009	0.497
Calcium	$CaCl_2.6H_2O$	500	0.506	0.011	0.495
Cerium	$Ce(SO_4)_2.4H_2O$	500	0.021	0.001	0.020
Chromium	$Cr(NO_3)_3,9H_2O$	500	0.145	0.001	0.144
Cobalt	$CoCl_2.6H_2O$	500	0.513	0.016	0.497
Copper	$CuSO_4.5H_2O$	10	0.510	0.014	0.496
,,	,,	100	0.575	0.084	0.491
Gallium	$CsGa(SO_4)_2.12H_2O$	250	0.510	0.014	0.496
Indium	$In_2O_3 + KHSO_4$	250	0.935[b]	0.440[b]	0.495
Iron	$FeSO_4.7H_2O$	500	0.529	0.031	0.498
,,	$NH_4Fe(SO_4)_2.12H_2O$[c]	3	0.351	0.010	0.341
,,	$NH_4Fe(SO_4)_2.12H_2O$[d]	30	0.485	0.010	0.475
,,	$NH_4Fe(SO_4)_2.12H_2O$[e]	100	0.527	0.032	0.495
Lead	$Pb(NO_3)_2$	500	0.510[a]	0.000[a]	0.510
Lithium	Li_2CO_3+HCl	500	0.507[f]	0.018[f]	0.489
Magnesium	$MgSO_4.7H_2O$	500	0.504	0.010	0.494
Manganese	$MnCl_2.4H_2O$	500	0.502	0.007	0.495
Mercury	$HgCl_2$	500	0.509	0.010	0.499
Nickel	$NiSO_4.7H_2O$	500	0.528	0.033	0.495
Rubidium	Rb_2SO_4	500	0.515	0.013	0.502
Sodium	$NaCl$	1000	0.509	0.014	0.495
Strontium	$SrCl_2.6H_2O$	500	0.504[a]	0.008[a]	0.496
Thallium	$TlNO_3$	500	0.502	0.007	0.495
Thorium	$Th(NO_3)_4.4H_2O$	500	0.498	0.017	0.481
Uranium	$UO_2(C_2H_3O_2)_2.2H_2O$	500	0.514	0.038	0.476
Zinc	$ZnSO_4.7H_2O$	500	0.505	0.011	0.494

[a] Optical density measurements made on filtered solutions.
[b] Optical density measurements after subtracting blank for silicon in $KHSO_4$.
[c] In $0.01N$ H_2SO_4.
[d] In $0.10N$ H_2SO_4.
[e] Reduced with 1 ml of 10% hydroxylamine hydrochloride before addition of acid molybdate.
[f] Optical density measurements after subtracting blank for silicon in hydrochloric acid.

Oxidizing agents such as chlorates, iodates and ceric-cerium reduce the intensity of the colour formed.

Of the elements forming reducible heteropoly acids only phosphorus, germanium and vanadium interfere appreciably. Wavelengths of maximum absorption of

TABLE IX

INTERFERENCE OF ANIONS ON DETERMINATION OF 4 μg SILICON

Anion	Added as	Concentration of element in p.p.m.	Optical density		
			4 μg Si	Blank	Difference
Acetate	$CH_3CO_2NH_4$	500	0.510	0.014	0.496
Arsenate	$Na_2HAsO_4 . 7H_2O$	4	0.510	0.010	0.500
"	"	100	0.417	0.048	0.364
Arsenite	$As_2O_3 + NaOH$	4	0.506*	0.009*	0.497
"	"	100	0.562*	0.077*	0.485
Borate	H_3BO_3	500	0.504	0.006	0.498
Bromide	KBr	500	0.528	0.031	0.497
Chlorate	$KClO_3$	500	0.497	0.003	0.494
Chloride	KCl	1000	0.508	0.014	0.494
Cyanide	KCN	500	0.539	0.042	0.497
Dichromate	$K_2Cr_2O_7$	500	0.488	0.004	0.484
Ferrocyanide	$K_4[Fe(CN)_6] . 3H_2O$	500	0.675	0.190	0.485
Fluoride	NaF	0.80	0.532	0.030	0.502
"	"	10	0.548	0.052	0.496
"	"	50	0.709	0.226	0.483
"	NaF + 1 ml 0.1 $N H_3BO_3$	50	0.712	0.221	0.491
Germanate	$GeO_2 + Na_2CO_3$	0.5	0.791	0.290	0.501
Iodate	KIO_3	500	0.479	0.008	0.471
Iodide	KI	500	0.508	0.010	0.498
Nitrate	KNO_3	500	0.512	0.013	0.499
Perrhenate	$KReO_4$	500	0.526	0.029	0.497
Phosphate	KH_2PO_4	5	0.509	0.012	0.497
Sulphate	K_2SO_4	500	0.504	0.008	0.496
Thiocyanate	KCNS	500	0.506	0.005	0.501
Vanadate	NH_4VO_3	15	0.727	0.228	0.499

* Optical density measurements after subtracting blank for silicon in NaOH.

their molybdenum blue complexes are 818 mμ, 820 mμ and 810 mμ respectively.

The optical density of the molybdenum blue formed from phosphomolybdic acid by metol (measured after 3 hours) is only *ca.* 9.5% of that found from an equivalent amount of silicomolybdic acid. The interference of phosphorus can be reduced still further by the addition of oxalic acid at the time of the reduction of the complex as suggested by SCHWARTZ[47]. The effect of oxalic acid on the colour developed with 40 μg PO_4-P in 20 ml of water has been investigated. The process described for the determination of silicon was used, but the 10% oxalic acid was omitted from the reducing agent and added separately in varied amounts. The results shown in Table X illustrate the remarkable suppression of the colour by oxalic acid, although small amounts of the acid enhance the colour. The colour intensity from silicon is not affected. Concentrations of up to 5 p.p.m. of PO_4-P, cause no error in the determination of 0.2 p.p.m. of silicon, but above this level the colour from the silicon is much reduced owing perhaps to insufficient excess of ammonium molybdate.

TABLE X

ml of 10% oxalic acid	0	0.25	0.5	1.0	2.0	3.0	4.0
Optical density* after							
3 hours	0.479	0.748	0.798	0.096	0.007	0.004	0.003
16 hours	0.938	1.374	0.943	0.096	0.008	0.003	0.005

* 40 μg PO_4-P measured at 812 mμ in 7.62 cm cell.

It is relevant here to mention the importance of cleaning the graduated flasks used for the determination of silicon with a mixture of nitric and sulphuric acids. Spuriously high results were frequently obtained with flasks which had been previously used for the determination of phosphate and afterwards merely washed with distilled water.

The interference of germanium is potentially more serious, since germanomolybdic acid is reduced to molybdenum blue in the presence of oxalic acid. Its colour intensity is, however, only about 22% of that obtained with the same weight of silicon, so that the amounts of germanium normally encountered in natural waters (less than 1 μg/l) will not cause any appreciable error. The colour formed by vanadate-vanadium in the presence of oxalic acid is only 1/173 of that formed by silicon.

Fluoride in large amounts (above 50 p.p.m.) diminishes the amount of molybdenum blue formed. Its interference can be much reduced by addition 1 ml of 0.1*N* boric acid[48] as a complexing agent prior to the addition of the acid-molybdate reagent.

Application of the method to sea-waters

When the proposed method was applied to sea-waters, it was found that maximum colour was developed in approximately 60 minutes, and that no fading occurred for at least 24 hours. The dissolved salts of the sea-water reduce the final colour intensity appreciably. In order to determine the salt error, waters of known chlorinity were prepared by dilution of a filtered water from the Irish Sea (Cl = 18.979$^0/_{00}$); 20 ml samples of each of these waters were enriched by the addition of increments of from 0.5 to 4.0 μg silicate-silicon and the silicon determined. It was found that Beer's law was obeyed over this range of concentrations. The variation of salt error with chlorinity is linear and is shown in Table XI; each value is the mean of 7 determinations.

The true optical density (D) of a silicate determination in sea-water may be calculated from the equation

$$D = D_0\ (1 + 0.00578\ \text{Cl}).$$

Where D_0 is the observed optical density at 812 mμ and Cl is the chlorinity of the sample. For many purposes where ocean waters are examined it is sufficient to employ a correction factor of 1.1.

TABLE XI

Chlorinity (Cl°/₀₀)	0	2.37	4.75	9.49	14.24	18.98
Optical density increment for 1 μg Si*	0.1250	0.1232	0.1218	0.1186	0.1155	0.1128
Salt error %	0.0	—1.4	—2.6	—5.1	—7.6	—9.8

* Measured in 7.62 cm cell.

To obtain the greatest accuracy in the analysis of normal sea-waters it is advisable to employ a sample of only 15 ml and to add *ca.* 5 ml of distilled water before addition of the acid molybdate reagent. If determinations are made directly on undiluted sea-water the precision of the method is somewhat reduced. This is in accordance with the findings of STRICKLAND[20] that concentrations of foreign ions greater than 0.5*M*, caused the formation of variable amounts of *α*-silicomolybdic acid.

The precision of the method has been tested by carrying out replicate analyses of sea-water samples enriched with known amounts of silicate-silicon. A standard deviation of 0.48% was attained with concentrations of silicon of *ca.* 0.2 p.p.m.

SUMMARY

The optimum conditions for the determination of silicate in natural waters by a molybdenum blue method have been investigated. *p*-Methylaminophenol sulphate has a number of advantages over other reducing agents for the reduction of silicomolybdic acid to molybdenum blue. BEER's law is obeyed up to concentrations of at least 3 mg/l.

The interference of several inorganic ions has been investigated; none of those encountered in natural waters is likely to cause error. The method has been applied to the analysis of sea-water and the "salt error" correction evaluated.

RÉSUMÉ

Les conditions optima de dosage de silicate dans les eaux normales par la méthode au bleu de molybdène ont été examinées. Le sulfate de *p*-méthylaminophénol présente un certain nombre d'avantages sur les autres réducteurs utilisés pour la réduction de l'acide silicomolybdique en bleu de molybdène. La loi de BEER est suivie pour des concentrations allant au moins jusqu'à 3 mg/l. L'influence de divers ions inorganiques a été examinée, aucun de ceux présents dans les eaux naturelles ne gêne. Cette méthode a été appliquée à l'analyse de l'eau de mer.

ZUSAMMENFASSUNG

Es wurden die optimalen Bedingungen gesucht für die Bestimmung von Silikat im natürlichen Wasser mit der Molybdenblaumethode. Das Sulfat von *p*-methylaminophenol weist eine gewisse Anzahl Vorteile auf gegenüber den andern Reduktionsmitteln, welche für die Reduktion der Silicomolybdänsäure zu Molybdänblau verwendet werden. Das BEER'sche Gesetz findet Anwendung für Konzentrationen, die mindestens bis zu 3 mg/l gehen. Der Einfluss von verschiedenen anorganischen Ionen wurde geprüft. Keines der im natürlichen Wasser vorkommenden Ionen stört die Bestimmung. Diese Methode wurde verwendet für die Analyse des Meerwassers.

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POTENTIOMETRIC TITRATION OF LOW CONCENTRATIONS OF BORIC ACID ANHYDRIDE IN DEUTERIUM OXIDE AND IN ORDINARY WATER*

by

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RUEHLE AND SHOCK[1] titrated boric acid in aqueous magnesium chloride solutions, using the potentiometric null point method. In the range of 10 to 50 mg of boric acid the results were satisfactory for their purpose, although errors of 10 per cent or more were found when only 10 mg of boric acid are present. HOLLANDER AND RIEMAN[2], however, found that boric acid could be titrated in mannitol solutions using phenolphthalein as indicator. The object of their study was to ascertain the correct amount of mannitol for this titration, but the concentrations of the boric acid solutions were reasonably high, $0.057M$ (3.4 g per liter).

In the present work it was proposed to determine boron, as boric acid anhydride, in solutions as low as $7.2 \cdot 10^{-4}M$. A precision of 99.5 per cent was sought, and the solvent could be either water or deuterium oxide.

Boric acid anhydride dissolves in water as H_3BO_3 and in deuterium oxide as D_3BO_3. Either form is expected to complex with glycerin or mannitol and react as a monobasic acid, but since the properties of deuterium oxide differ from that of ordinary water it is desirable to investigate and to show that the potentiometric titration method is applicable.

Titrations were performed in aqueous solutions as reference method, then duplicated in deuterium oxide. Both glycerol and mannitol were used as complexing agents; solutions were pre-boiled under reflux and then helium was used to purge the solution and also to stir the solution. Nitrogen is unsatisfactory as a purge gas because it contains uncertain quantities of carbon dioxide.

APPARATUS AND CHEMICALS

Beckman pH meter fitted with glass and calomel electrodes.

Mannitol (neutral, boric acid-free) - $CH_2OH-(CHOH)_4-CH_2OH$.

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Glycerine, c.p. - $C_3H_5(OH)_3$.
Helium gas - grade A.
Barium chloride, c.p., anhydrous - $BaCl_2$.
Boric acid, reagent grade - H_3BO_3.
Boric acid anhydride, purified - B_2O_3.
Standard boric acid solutions:

- 0.0015*M* boric acid (0.00075*M* boric acid anhydride). Weigh 180 mg of boric acid, dissolve in distilled water and dilute to two liters.
- 0.003*M* boric acid (0.0015*M* boric acid anhydride). Weigh 360 mg of boric acid, dissolve in distilled water and dilute to two liters.

Boric acid anhydride solution in deuterium oxide. Heat 67.5 g of boric acid anhydride at 400° C for 4 hours to remove moisture (about 2 g). Cool in a dry box and dissolve in 3 liters of deuterium oxide. Make appropriate dilutions with deuterium oxide as dilutant and check by titration.

Potassium hydroxide, c.p.
Standard potassium hydroxide solutions:

- 0.015*N* potassium hydroxide — Make a saturated solution of potassium hydroxide in water (25 g per 25 ml), allow the carbonate to settle, then decant about 0.6 ml (0.6 g KOH) into distilled water and dilute to one liter. Add about 0.1 g barium chloride and allow to stand for one day. Standardize against boric acid as described in the procedure.
- 0.030*N* potassium hydroxide — Similar to 0.015*N* potassium hydroxide, except that 1.2 ml (1.2 g KOH) is used.
- 0.005*N* potassium hydroxide — Dilute one volume of 0.030*N* potassium hydroxide with five volumes of water.

EXPERIMENTAL

General survey

Type of sample: B_2O_3 dissolved in D_2O (or H_2O).
Concentration of B_2O_3: 0.76 to 150 mg per liter ($1.1 \cdot 10^{-5}$ to $21.6 \cdot 10^{-4}$ mol).
Sample size: 200 ml aliquot (2 to 30 mg B_2O_3).
250 ml aliquot (0.2 to 2 mg B_2O_3).
Titrant: Potassium hydroxide
0.005*N* KOH for 0.76 to 2 mg B_2O_3/l
0.015*N* KOH for 2 to 75 mg B_2O_3/l
0.030*N* KOH for 25 to 150 mg B_2O_3/l

Titrations with glycerol

Experimental samples were made to contain 25 mg, 50 mg, 75 mg, etc. ($3.6 \cdot 10^{-4}$, $7.2 \cdot 10^{-4}$, $1.1 \cdot 10^{-3}$ mol, etc.) B_2O_3 per liter of distilled water. The test samples of 200 ml would then contain 5 mg, 10 mg, 15 mg, etc. respectively, of B_2O_3

per titration. Glycerol, in known amounts (25 ml to 50 ml) was added as complexing agent. Potentiometric titrations, as described in the procedure, were then performed with appropriate standard alkali solutions. Further, test runs were made on solutions with or without preliminary refluxing, and with or without purging by helium during the analysis. Tests were also made in which the solvent was deuterium oxide.

Titrations with mannitol

Experimental determinations were made as described with glycerol, except that known weights of mannitol were substituted for the liquid glycerol. The weights of the mannitol additions were varied from 2 to 20 grams. Concentrations of B_2O_3, as low as 0.76 mg/l (0.19 mg per 250 ml sample) were titrated.

The pH's and slopes of the curves at the equivalence point were noted.

RESULTS AND DISCUSSION

The experience gained from the present experimental work shows that dilute boric acid solutions must be boiled, purged with carbon dioxide-free gas before titration and stirred with the same gas during the titration (except while taking readings). By observing these precautions, titrations proceed smoothly. In addition it must be kept in mind that boric acid can be distilled from solutions of low pH. Hence, the boiling of boric acid solutions must be performed under reflux condenser. We have also noted that alkaline aqueous solutions which have been heated in so-called "boron-free" glassware will extract 0.002 mg of boron from the container.

Potentiometric titrations of dilute solutions of boric acid with standard alkali are difficult to perform. The point of inflexion is in the neighbourhood of pH 11, and the exact location is sometimes in doubt.

Certain polyhydroxy alcohols and sugars react with boric acid to form ionically strong complex acids. The potentiometric titrations of such boric acid solutions with standard alkali resemble the titrations of the more familiar mineral acids. The point of inflexion is below pH 9, and the exact location is easily ascertained.

The pH (hydrogen-ion) of ordinary water (protium oxide) differs from the pD (deuterium-ion) of heavy water (deuterium oxide). When the acidity of pure heavy water is read with a standard pH meter, the reading is about 0.3 units lower than that obtained from a Rosser-type[3] pD meter.

In mixtures of light and heavy waters, neither meter functions correctly, but readings obtained by either instrument are relatively correct when indicating acidity changes in a particular mixed solution. For this reason potentiometric titrations may be followed by either meter in heavy water, ordinary water or their mixtures.

Comparative titrations of 10 mg of boric acid anhydride in 200 ml of water were made with 15 grams of mannitol and with 25 ml of glycerol. The slope of the curve at the inflexion point (Fig. 1) indicated that mannitol would be preferable to glycerol; furthermore, the pH with mannitol was appreciably lower (8 *vs* 8.6).

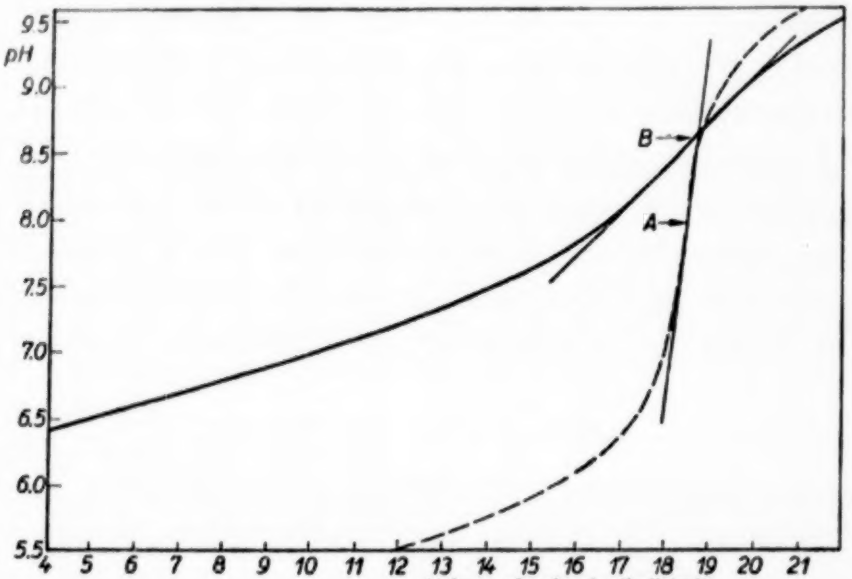

Fig. 1. Titration of 50 mg/l boric acid anhydride in water. 200 ml volume (10 mg B_2O_3)

A Mannitol (15 g)		B Glycerol (25 ml)	18.70 ml
Volume of KOH	18.50 ml	Volume of KOH	18.70 ml
N of KOH	0.01565	*N* of KOH	0.0155
Inflection	7.98 (pH meter)	Inflection	8.65 (pH meter)
Slope	2.5	Slope	0.40

TABLE I

EFFECT OF MANNITOL CONCENTRATION ON TITRATION OF BORIC ACID ANHYDRIDE IN 200 ml H_2O

Boric acid taken (mg/l)	B_2O_3 Equivalent (mg/l)	Mannitol taken (g)	Slope at equivalence point (ΔpH/ml)	pH at equivalence point
53.78	30.28*	20	50.	7.92
53.78	30.28	20	5.0	7.89
53.78	30.28	20	5.0	7.88
53.78	30.28	15	4.2	7.98
53.78	30.28	10	2.5	8.33
53.78	30.28	5	2.0	8.24
53.78	30.28	3	1.25	8.75
53.78	30.28	2	0.62	9.06

* 30.28 mg/l B_2O_3 = $4.35 \cdot 10^{-4}$ mol/l

Fifty ml of glycerol, instead of 25 ml, did not improve the slope of the titration curve. Table I shows that the equivalence point is located at pH 8 and that the sharpest slope is obtained with a concentration of 20 g of mannitol per 200 ml of solution.

Similar runs were made with boric acid anhydride dissolved in deuterium oxide, and the results are shown graphically in Figs. 2 and 3. The presence of mannitol in the boric acid anhydride-deuterium oxide solution accounts for the lower pH neutralization point in Fig. 3. Table II shows that the equivalence point in deuterium oxide (at pH 8) is similar to that obtained in light water.

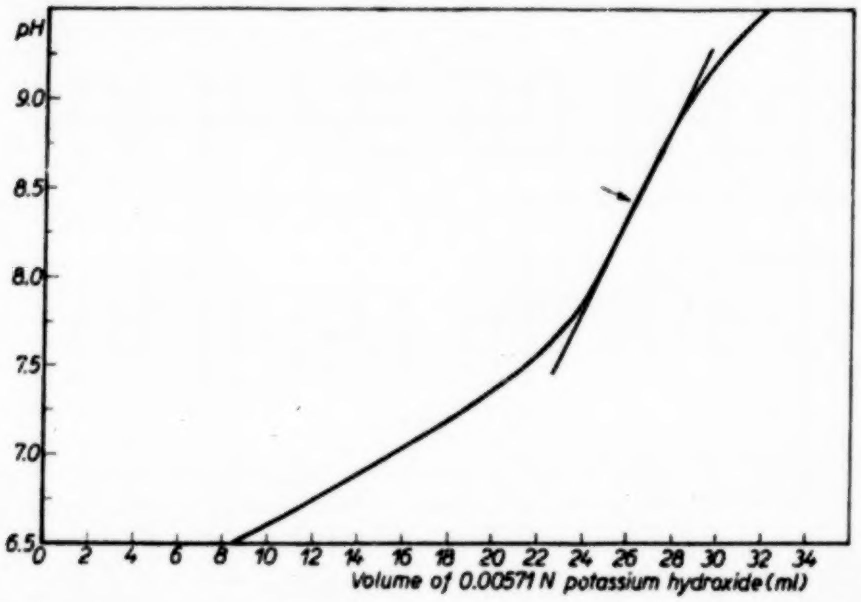

Fig. 2. Titration of 50 mg boric acid anhydride/liter of deuterium oxide.

Volume of KOH	26.35 ml	Volume of B_2O_3 solution	100 ml
N of KOH	0.00571	Weight of B_2O_3	5 mg
Inflection	8.40 (pH meter)	Volume of glycerol	25 ml
Slope	0.30		

TABLE II

TITRATION OF BORIC ACID ANHYDRIDE IN 200 ml D_2O*

B_2O_3 (mg)	Mannitol (g)	Slope at equivalence point (ΔpH/ml)	pH at equivalence point
47.0	20	1.75	7.95
47.0	20	2.00	8.08
47.1	20	2.00	7.99

* The D_2O contained 99.8 atom — % D

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TABLE III

TITRATION OF SMALL CONCENTRATIONS OF BORIC ACID IN WATER WITH POTASSIUM HYDROXIDE IN THE PRESENCE OF MANNITOL

Batch	H_3BO_3 (mg taken)	Equivalent B_2O_3 (mg taken)	H_2O (ml taken)	Vol. KOH used (ml)	B_2O_3 found (mg)	Error (taken-found) (mg)	Per cent error*	Standard deviation (mg)	Per cent. deviation**
1	44.53	25.06	200					±0.030	±0.12
				22.90	25.12	—0.06	—0.24		
				22.90	25.12	—0.06	—0.24		
	44.62	25.11	200	22.90	25.12	—0.01	—0.04		
				22.95	25.18	—0.07	—0.28		
2	35.63	20.05	200	18.15	20.04	+0.01	+0.05	±0.025	±0.12
				18.20	20.09	—0.04	—0.20		
				18.15	20.04	+0.01	+0.05		
				18.15	20.04	+0.01	+0.05		
3	17.93	10.10	200	18.50	10.08	+0.02	+0.20	±0.031	±0.28
				18.60	10.14	—0.04	—0.39		
				18.50	10.08	+0.02	+0.20		
				18.50	10.08	+0.02	+0.20		
4	3.42	1.93	250	8.90	1.94	—0.01	—0.91	±0.014	±0.73
				8.85	1.92	+0.01	+0.91		
5	0.34	0.19	250	1.20	0.19	0.00	0.00	±0.010	±5.26
				1.24	0.20	—0.01	—11.00		
				1.15	0.18	+0.01	+11.00		

* Per cent error $= \dfrac{\text{mg taken} - \text{mg found}}{\text{mg taken}} \times 100$

** Per Cent Deviation $= \dfrac{\text{standard deviation in "mg } B_2O_3\text{" found}}{\text{total "mg } B_2O_3\text{" found}} \times 100$

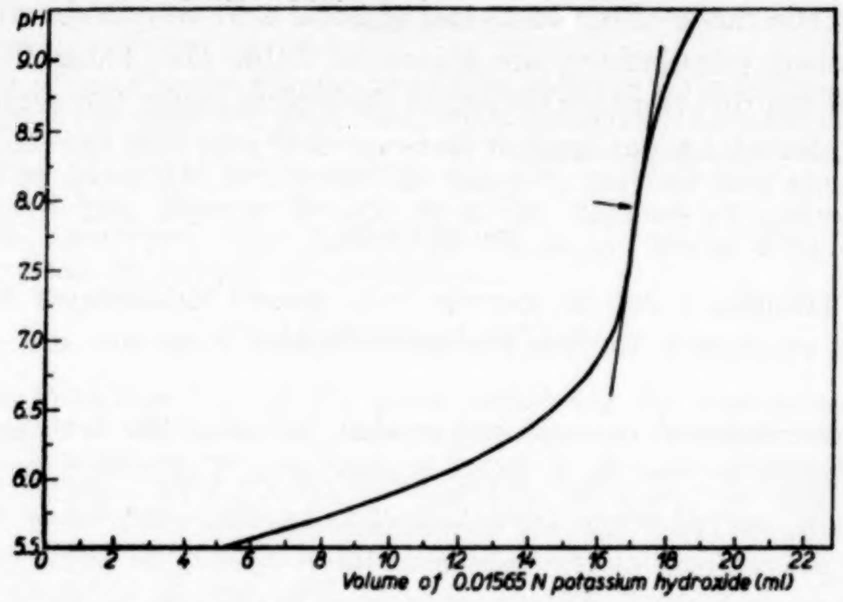

Fig. 3. Titration of 50 mg boric acid anhydride/liter of deuterium oxide.

Volume of KOH	17.3 ml	Volume of B_2O_3 solution	100 ml
N of KOH	0.01565	Weight of B_2O_3	10 mg
Inflection	7.95 (pH meter)	Weight of mannitol	15 g
Slope	1.80		

TABLE IV

TITRATION OF SMALL CONCENTRATIONS OF BORIC ACID ANHYDRIDE IN DEUTERIUM OXIDE* WITH POTASSIUM HYDROXIDE IN THE PRESENCE OF MANNITOL (200 ml VOLUME)

Batch	B_2O_3 found (mg)	Vol. KOH used (ml)	Per cent deviation	Standard deviation in ml KOH	Standard deviation in mg B_2O_3
1	29.33	26.75	±0.31	±0.09	±0.09
	29.33	26.75			
	29.28	26.70			
	29.50	26.90			
2	24.78	22.60	±0.37	±0.10	±0.09
	24.78	22.60			
	24.56	22.40			
	24.67	22.50			
3	19.54	17.70	±0.15	±0.03	±0.03
	19.54	17.70			
	19.59	17.75			
4	14.46	26.55	±0.15	±0.04	±0.02
	14.44	26.50			
	14.46	26.55			
	14.48	26.60			
5	9.40	17.25	±0.48	±0.09	±0.045
	9.31	17.10			
	9.40	17.25			
	9.42	17.30			

* Deuterium oxide, 99.8 per cent deuterium.

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Titrations in the range of 0.2 to 25 mg of boric acid anhydride with attendant standard deviation calculations, are shown in Table III. Table IV summarizes a group of precision titrations performed in deuterium oxide, the average deviation being of the order of 0.5 per cent or less.

PROCEDURE

By pipette, transfer a 200-ml sample to a 300-ml Erlenmeyer flask and boil under a reflux condenser for ten minutes. Protect from air and cool to room temperature.

Place 20 g of mannitol in a 400-ml beaker, transfer the test solution to the beaker and bubble in helium gas to purge the solution. The helium is used throughout the titration, except when potentiometric readings are being made.

Record the pH reading of the solution which should be between 5 and 6, if no alkali is present. Add the titrant, potassium hydroxide, in sufficient amounts to raise the pH in steps of about 0.5 units until a pH of 7 is neared, recording all the readings. Decrease the increments to 0.05 to 0.2 ml of titrant (depending on its concentration), recording the readings until a pH of 9 is reached, or past.

Plot volume of titrant as abscissa and pH as ordinate on regular cross-section paper. Measure for the point of inflection of the curve to obtain the titration value.

From the equations, based on H_2O or D_2O as solvent:

$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3,\ 2H^+ + 2\ [H_2BO_3\ \text{Complex}] \quad \ldots\ldots\ldots \quad (1)$$

or

$$B_2O_3 + 3D_2O \rightarrow 2D_3BO_3,\ 2D^+ + 2\ [D_2BO_3\ \text{Complex}] \quad \ldots\ldots\ldots \quad (2)$$

calculate B_2O_3, equivalent to a dibasic acid.

$$B_2O_3\ (\text{mg}) = \text{ml titrant} \times N \text{ of titrant} \times 34.82\ \text{mg/ml} \quad \ldots\ldots \quad (3)$$

CONCLUSIONS

Low concentrations of boric acid anhydride in deuterium oxide can be titrated with standard alkali provided there is sufficient mannitol present and all solutions are carbonate free. Glycerol (up to 20 per cent by volume) is not satisfactory as complexing agent for boric acid anhydride.

The error in titration is ± 0.5 per cent in concentrations of boric acid anhydride as low as $7.2 \cdot 10^{-4} M$, and 5 per cent in concentrations of boric acid anhydride as low as $1.1 \cdot 10^{-5} M$.

SUMMARY

A precision of 99.5 per cent, or better, is obtainable for the determination of boric acid anhydride (50 to 150 mg per liter) in deuterium oxide or ordinary water solution; titrations may be performed with concentrations as low as 0.76 mg per liter. Sufficient mannitol is added so that the potentiometric curve is duplicable. Glycerol is not satisfactory, in deuterium oxide, at low molar concentrations of boric acid anhydride.

Differences in pH end-points for water and deuterium oxide solutions were noted.

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RÉSUMÉ

Une précision de 99.5% (ou mieux) peut être obtenue pour le dosage de l'anhydride borique (50 à 150 mg/litre) dans l'oxyde de deutérium ou dans l'eau ordinaire; des titrations peuvent être effectuées avec de faibles concentrations allant jusqu'à 0.76 mg/litre. Des quantités suffisantes de mannite doivent être ajoutées. La glycérine ne convient pas, pour le dosage de faibles teneurs en anhydride borique dans l'oxyde de deutérium. Des différences de pH au point d'équivalence sont observées entre l'eau et l'oxyde de deutérium.

ZUSAMMENFASSUNG

Es kann eine Präzision von 99.5% (oder mehr) für die Bestimmung von Borsäureanhydrid (50-150 mg/l) im Deuteriumoxyd oder in gewöhnlichem Wasser erhalten werden. Titrationen können mit schwachen Konzentrationen bis zu 0.76 mg/l ausgeführt werden. Eine genügende Quantität Mannit muss beigefügt werden. Glycerin eignet sich nicht im Deuteriumoxyd für die Bestimmung von kleinen Quantitäten von Borsäureanhydrid. Im Gleichgewichtspunkt wurden Unterschiede des pH-Wertes zwischen Wasser und Deuteriumoxyd festgestellt.

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[2] M. Hollander and W. Rieman III, *ibid.*, (1945) 602.
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THE ANALYSIS OF COMBUSTION PRODUCTS

IV. THE POLAROGRAPHIC DETERMINATION OF THE LOWER ORGANIC PEROXIDES

by

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INTRODUCTION

Previous studies of the polarographic behaviour of organic peroxides have been concerned either with the analysis of combustion products of the lower hydrocarbons (STERN AND POLAK[1], NEUMANN AND DOBRINSKAJA[2] AND NEUMANN AND GERBER[3]), or with the autoxidation or polymerization products of large molecules (BOVEY AND KOLTHOFF[4], SWERN, KNIGHT *et al*[5]). The latter were carried out mainly in organic solvents, and are not directly relevant to the present work. The results of the earlier authors[1,2,3] were not sufficiently extensive for the present series of investigations, in which it was necessary to be able to analyse and differentiate mixtures of hydrogen peroxide, acyl hydroperoxides and various alkyl peroxides. The analysis of these compounds when formed in the reaction products has proved to be difficult in the past, since purely chemical methods were not able to identify the individual peroxides. This communication describes the polarographic behaviour of hydrogen peroxide, methyl-, ethyl-, and *t*-butylhydroperoxides, di-ethyl peroxide, and the three lowest acyl hydroperoxides, and some methods for dealing with mixtures. The influence of aldehydes is also considered.

EXPERIMENTAL

The polarograms were obtained with a recording Tinsley Polarograph, model 13/2. The potential scale of this could be enlarged five times. Potentials were checked and pH's measured with a Doran pH meter.

Cell

This is shown in Fig. 1. An external saturated calomel electrode (S.C.E.) *R* was connected by a wide bridge *B* (of low resistance) to the polarographic cell itself, through a plug of gelatin *G* which had been soaked in lithium sulphate

Preliminary experiments suggested that agar-agar, gelatin and sintered glass (which are often used in polarographic cells) could cause decomposition of the peroxide solution. The plug of gelatin was therefore placed in the bridge in such a way that any decomposition would be localized, and not affect the polarographic results. The area of mercury exposed to peroxides was made as small as possible by letting the mercury drops fall into an appendix *A* of less than 0.5 cm diameter. No decomposition was observed while the analyses were being carried out.

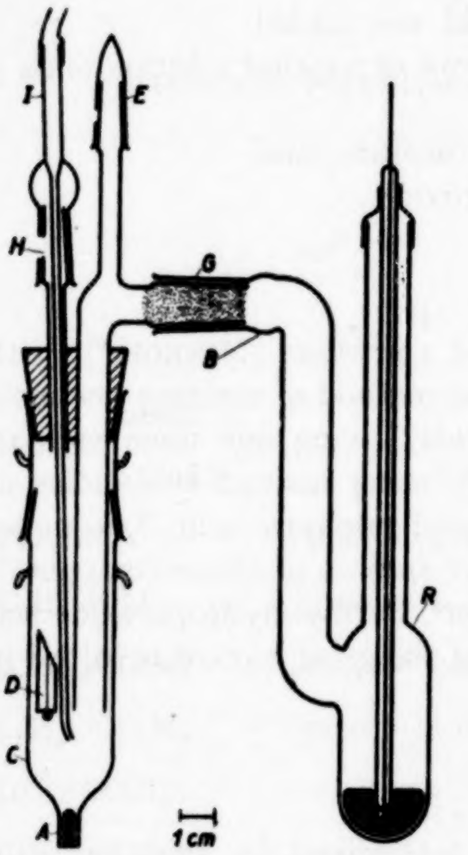

Fig. 1. Polarographic cell.

The cell *C* was filled with approximately 15 ml of the solution containing the electrolyte and the peroxide, and then immersed in a thermostat at $25.00 \pm 0.05°$ C. To remove dissolved oxygen, nitrogen (oxygen-free) was passed through inlet tube *I*, which was so placed with respect to the end of the bridge that the liquid in this limb was displaced by the nitrogen. The hole in the joint under the cap over *E* was closed, so that nitrogen now escaped through *H*, a hole in the joint carrying the nitrogen inlet tube. After 7-10 minutes *E* was opened and *H* was closed by turning the inlet tube *I*, forcing liquid up the bridge, to the level of *E*. The nitrogen flow was then stopped, and *E* closed.

The cell had an internal resistance (with $0.1M$ Li_2SO_4) of 2440 ohms, which was measured with a Mullard HF bridge.

The dropping electrode ***D*** had the following characteristics:

m = 1.38 mg sec^{-1} (mercury flow through capillary).
$t = 3.9 \pm 0.2$ sec (drop time with open circuit, in $0.1M$ Li_2SO_4).
$m^{2/3} \times t^{1/6} = 1.56$.
h = 55.0 cm (height of mercury reservoir).

The values selected were found to give a horizontal limiting diffusion current with the lower peroxides. Faster flows of mercury resulted in a decrease in current with increasing voltage, while a slight increase was observed with a longer drop time.

Materials

Lithium sulphate ($0.1M$) was finally selected as supporting electrolyte, since the lithium cation gave a large negative potential range, which permits the determination of aldehydes, and also because the peroxides are stable in this medium. The substance to be analysed was made up to exactly 25 ml with the amounts indicated below of the appropriate stock solutions:-

0.5M lithium sulphate (AnalaR) (5 ml) for all solutions.

0.1M lithium hydroxide (2.6 ml) or 1M (1 ml) according to the alkalinity required. These solutions were obtained by dissolving pure lithium metal in water.

For acid solutions, 1 ml of 0.1N sulphuric acid was added.

When a maximum suppressor was required, 3 drops of napthol solution (0.02 g in 50 ml water) were used.

Lanthanum reagent: 1 ml of 0.2M lanthanum acetate, and
1 ml of 1M lithium hydroxide.

Peroxides

These were prepared by the methods described elsewhere (MINKOFF[6]), with the exception of the acyl hydroperoxides. The usual method of reacting one mole of hydrogen peroxide with one of acetic anhydride, giving one mole each of acid and of acyl hydroperoxide was improved by using instead two moles of hydrogen peroxide and a large excess of concentrated sulphuric acid. Two moles of hydroperoxide were now formed. The refractive indices of these compounds were considerably higher than those reported earlier[6]. Formyl hydroperoxide was prepared only in dilute aqueous solution because of the great hazard involved in the purification (OLMOS[7]).

Chemical determination

The concentration of hydrogen peroxide was determined by titration with standard potassium permanganate solution in the presence of hydrochloric acid. Acetyl and propionyl hydroperoxides were determined according to the method of d'ANS[8], in which iodine is liberated instantaneously from an acidified, oxygen-free solution of potassium iodide at 0° C. Formyl hydroperoxide was determined by estimating the total peroxide content with potassium iodide in acid solution, in the presence of molybdate, and subtracting from this the amount of hydrogen peroxide indicated on the polarograms. Since there are no absolute quantitative methods for the determination of the (lowest) alkyl peroxides, the refractive indices shown in Table I were used as a criterion of purity (see Ref. 6 for a full discussion of this problem).

Measurement of limiting diffusion currents (i_d)

These were measured at fixed potentials (*vs.* S.C.E.), namely —0.20 V for acyl hydroperoxides (peracids), and —1.60 V for all other peroxides. The limiting diffusion current of the anodic step of hydrogen peroxide was measured at approximately -0.05 V. In order to obtain the correct values of i_d the residual of the supporting electrolyte was subtracted from the diffusion current observed. The position of the zero current was marked on each polarogram by disconnecting the cell from the polarograph.

TABLE I

HALFWAVE POTENTIALS (AT $i_d/2$); i_d/C AND D' VALUES AT 25° C

					0.1M Li_2SO_4					
	n_D^{20}		neutral			0.01M LiOH			0.004N H_2SO_4	
		$E_{½}$	i_d/C	D'	$E_{½}$	i_d/C	D'	$E_{½}$	i_d/C	D'
HOOH anodic					−0.11	6.12	0.88			
HOOH cathodic		−0.88	6.90	1.00	−1.03	6.12	0.88			
CH_3OOH	1.3608	−0.64	5.13	0.74	−0.95	4.15	0.65			
C_2H_5OOH	1.3798	−0.42	4.73	0.68	−0.60	4.36	0.63			
$(CH_3)_3COOH$	1.4007	−0.28	5.60	0.81	−0.30	5.45	0.79			
$C_2H_5OOC_2H_5$	1.3698	−0.65	4.75	0.69	−0.64	4.60	0.67			
HCO(OOH)	—							+0.2	8.1	1.2
$CH_3CO(OOH)$	1.4059							+0.2	7.12	1.03
$C_2H_5CO(OOH)$	1.4110							+0.2	6.20	0.90

Quantitative analysis

The limiting diffusion currents of individual peroxides were investigated in the range 10^{-5} to $3 \cdot 10^{-3} M$ and shown to be directly proportional to the peroxide concentration (Fig. 2). For a single substance, and with the same capillary, height of mercury level, temperature and electrolyte, the ILCOVIC equation reduces to:

$$i_d = K \cdot C \quad (C = \text{conc. in millimoles/l} \;\; K = \text{a constant})$$

The i_d/C values of a number of peroxides were determined from the calibration curves and are presented in Table I. Relative values of $(i_d/C)_{\text{peroxide } x} / (i_d/C)_{H_2O_2} = D'_x$ are also included in Table I, so that any other polarographic apparatus can be calibrated for peroxide analysis by running a polarogram of a known

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concentration of hydrogen peroxide in neutral solution. The concentration C_x of a peroxide x can then be found by the relation:

$$i_{dx} = K_{H_2O_2} \cdot D'_x \cdot C_x \ .$$

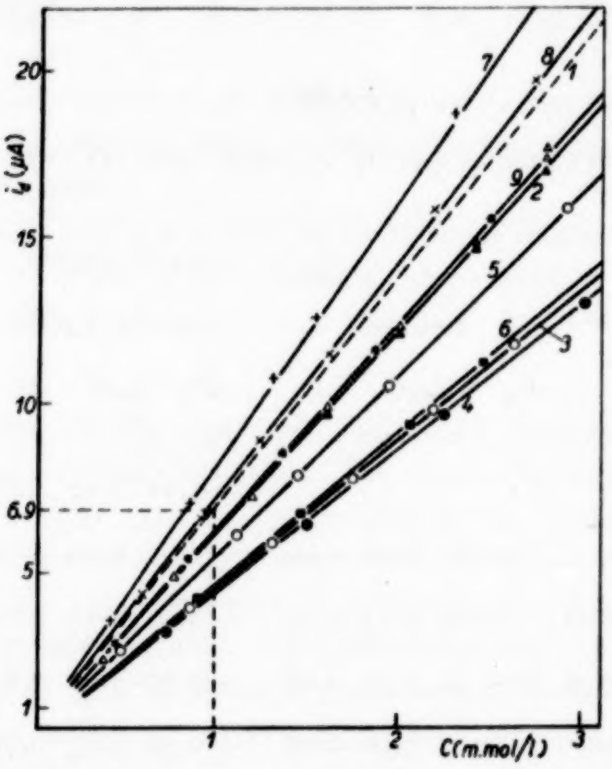

Fig. 2. Diffusion current (i_d) against concentration of peroxides.
1, hydrogen peroxide, neutral; 2, hydrogen peroxide, alkaline, △ anodic, ◆ cathodic; 3, methyl hydroperoxide; 4, ethyl hydroperoxide; 5, *tert.*-butyl hydroperoxide, alkaline; 7, performic acid; 8, peracetic acid; 9, perpropionic acid, acid solutions; supporting electrolyte: 0.1M lithium sulphate.

INDIVIDUAL PEROXIDES

Hydrogen peroxide

Hydrogen peroxide can be estimated polarographically in neutral, alkaline or acid solutions by using the drawn-out cathodic step with a halfwave potential of about —1.0 volts (*vs.* S.C.E.). In neutral and acidsolutions, the halfwave potential remains practically constant at —0.88 volts. The acid concentration should not exceed 0.01N, since the reduction of hydrogen ions then prevents the limiting diffusion-current from remaining constant.

In alkaline solutions, $E_{1/2}$ shifts to more negative values (Table II). At the same time, another, anodic step is observed, with $E_{1/2}$ = —0.1 volts, which rises much more steeply than the cathodic one (Fig. 3).

This anodic step is due to an electrochemical oxidation of hydrogen peroxide to molecular oxygen, and it is the reverse reaction of the well known reduction

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TABLE II

INFLUENCE OF pH ON CATHODIC STEP OF H_2O_2

pH	$E_{1/2}$ (at $i_d/2$)	D'
1.9	—0.87	1
2.2	—0.87	1
6.6	—0.88	1
11.3	—1.02	0.93
11.9	—1.21	0.90

of oxygen to hydrogen peroxide which causes the first cathodic step, at the same potential, in the polarograms of oxygen (BRÜSCHWEILER[9]). The anodic diffusion current $(i_d)_a$ becomes constant, and equal in magnitude to the cathodic diffusion current $(i_d)_c$, (though opposite in sign), when more than about 1.4 equivalents of alkali are present. The values of the two diffusion currents then remain equal to each other, even in the presence of a large excess of alkali (0.5*N* LiOH). With the alkaline electrolyte used (0.01*N* LiOH), the concentration of hydrogen peroxide to be analysed should not be greater than 3 millimole/l, since at higher concentrations of peroxide, $(i_d)_c$ tended to be slightly lower than $(i_d)_a$ (Fig. 2). It will be shown below that the anodic step of hydrogen peroxide is of importance in the analysis of mixtures of peroxides, since no other peroxide has such a step. The extended potential scale is normally used in order to separate the step more efficiently from the preceeding depolarization of HO^- ions.

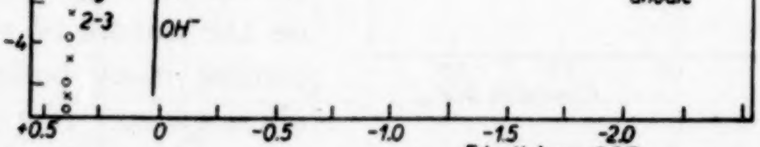

Fig. 3. Polarograms of hydrogen peroxide (0.326m*M*).
Polarogram 1 in alkaline solution.
Curve 2 xxxx in neutral solution.
Curve 3 oooo in acid solution.
Curve 4 ---- first cathodic step of oxygen.

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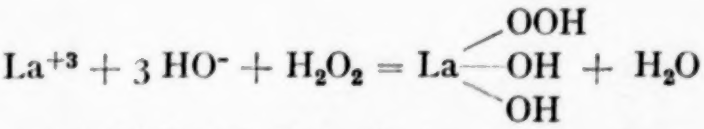
Lanthanum reagent: Attempts were made to precipitate hydrogen peroxide without affecting alkyl peroxides. The most satisfactory reagent for this purpose was a solution of a lanthanum salt, such as the acetate, which precipitated a basic lanthanum peroxide, $La(OH)_2OOH$ aq:



$$La^{+3} + 3\,HO^- + H_2O_2 = La\begin{cases}OOH\\OH\\OH\end{cases} + H_2O$$

This precipitate was stable in alkaline solutions. It dissolves partially in neutral, and entirely in acid, solutions. In alkaline solutions, the alkali being in excess, only the polarogram of the supporting electrolyte was obtained. It is essential to run the polarograms after de-oxygenation without delay, since the precipitate decomposes slowly to oxygen, which gives rise to a step. Peroxides which form an equilibrium with hydrogen peroxide, such as its hydroxy alkyl derivatives and acyl hydroperoxides, are also removed in the form of hydrogen peroxide. The use of the lanthanum reagent in alkaline solution thus provides a specific test for hydrogen peroxide and peroxidic compounds which are in equilibrium with hydrogen peroxide. Alkyl peroxides are left in solution.

Procedure: Hydrogen peroxide (1-10 ml of 0.01M) was made up to 25 ml, together with 5 ml of 0.5M lithium sulphate, 1 ml of 1N lithium hydroxide and 1 ml of 0.2M lanthanum acetate. When a polarogram was run, only the residual current was observed.

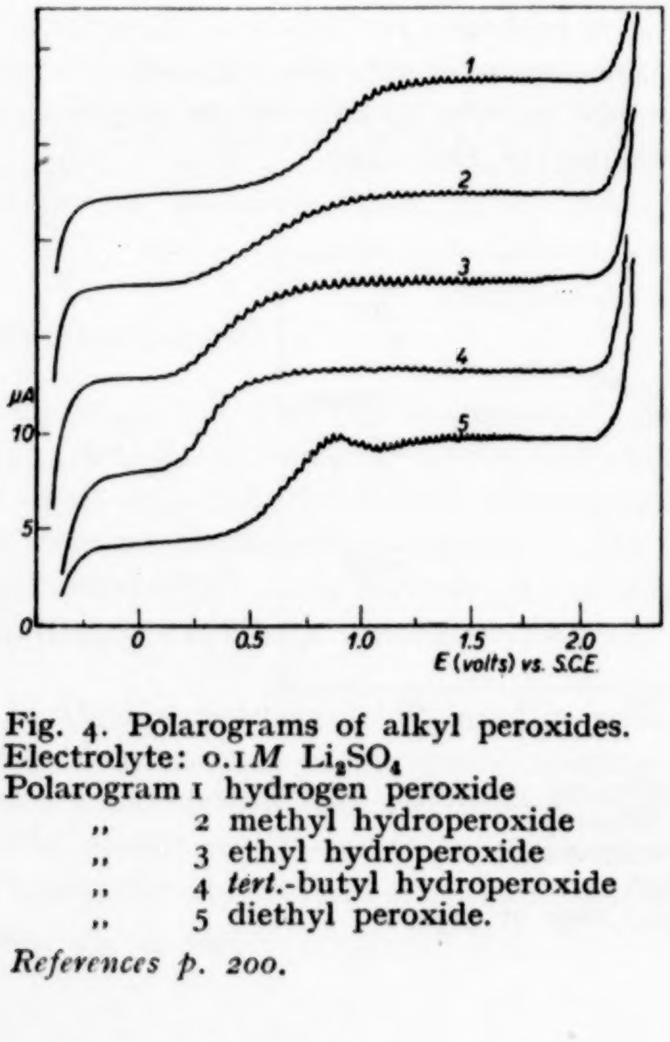


Fig. 4. Polarograms of alkyl peroxides.
Electrolyte: 0.1M Li_2SO_4
Polarogram 1 hydrogen peroxide
„ 2 methyl hydroperoxide
„ 3 ethyl hydroperoxide
„ 4 *tert.*-butyl hydroperoxide
„ 5 diethyl peroxide.

Alkyl hydroperoxides (ROOH)

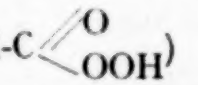
Alkyl hydroperoxides gave polarograms with shallow cathodic steps (Fig. 4), similar to that of hydrogen peroxide. The halfwave potential and the shape of the polarograms depend on the nature of the peroxide, becoming more positive with larger alkyl groups. More negative values are observed in alkaline solutions (Table I).

The halfwave potentials of these irreversible reductions are slightly affected by the characteristics of the capillary used. Alkyl hydroperoxides can be destroyed with titanium salts in alkaline solutions.

Di-alkyl peroxides (ROOR)

Di-*tert*.-butyl peroxide was not reduced, but satisfactory polarograms were obtained with di-ethyl peroxide. The halfwave potential was unaffected by change of pH. Solutions containing more than approximately 1 millimole/l yielded polarograms with a slight maximum (Fig. 4), which occurred over the whole pH range as well as in alcoholic solutions. It was replaced by a shoulder in the presence of naphthol. Since di-ethyl peroxide is very volatile, it must be added to the electrolyte in the cell after the passage of nitrogen, otherwise the peroxide is removed by the gas stream. The ease of replacement is comparable to that of oxygen.

Acyl Hydroperoxides (*Peracids*) (R-C$\begin{smallmatrix}\diagup O\\ \diagdown OOH\end{smallmatrix}$)



$R\text{-}C{\begin{array}{l}{}^{\diagup}O\\{}_{\diagdown}OOH\end{array}}$

It was found that these compounds can be determined polarographically in acidified solutions. The halfwave potentials were approximately +0.2 volts (*vs*. S.C.E.), being slightly more positive in solutions of lower pH, and with lower concentrations of peroxide. Propionyl hydroperoxide was found to be reduced at a slightly more positive potential than acetyl hydroperoxide and formyl hydroperoxide, but a distinction could not be made between different members of the series. They can, however, be differentiated from the lower alkyl peroxides.

The determination must be carried out in acid solutions. In neutral or alkaline solutions, badly defined waves, with irregular limiting diffusion currents, were observed. Satisfactory conditions were obtained in the presence of a small amount of acid (0.004N H_2SO_4), the limiting diffusion current being unaffected by change of pH in the acid range.

Pronounced maxima (*M*) (Fig. 5) were found between +0.1 to —0.4 volts, which

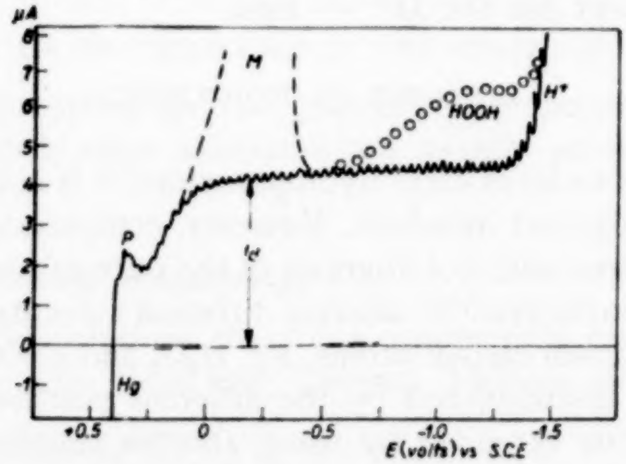


Fig. 5. Polarogram of propionyl hydroperoxide (0.625mM).
Electrolyte: 0.1M Li_2SO_4, 0.004N H_2SO_4,
$3 \cdot 10^{-6} M$ naphthol.
M: maximum without naphthol, *P*: peak

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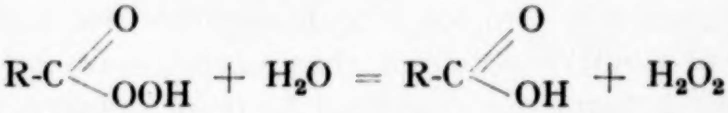
are completely suppressed by the addition of a trace of naphthol solution.

Another peak (*P*) occurred at *ca.* + 0.3 volts, which was unaffected by naphthol and was reproducible, independently of the direction in which the polarogram is run. The magnitude of this peak depends on the concentration of peracid, being pronounced at high concentration and absent at low concentration, (below *ca.* 0.3 millimole/l). The cathodic wave of the acyl hydroperoxides may then be continuous with the free anodic dissolution wave of mercury.

For satisfactory determinations, it is essential (a) to use a small mercury pool, in order to avoid decomposition, (b) to have a potential range, extending to positive as well as to negative values (*vs.* S.C.E.) and (c) to mark the position of the zero current on the polarograms. In the presence of chloride ions, which are anodically depolarized at about + 0.2 volts, a continuous anodic cathodic curve is observed.

Hydrolysis of acyl hydroperoxides

Acyl hydroperoxides hydrolyse in aqueous solution (d'Ans) according to the equation:



$$R\text{-}C\overset{O}{\underset{OOH}{}} + H_2O = R\text{-}C\overset{O}{\underset{OH}{}} + H_2O_2$$

The reaction occurs slowly with acetyl- and propionyl hydroperoxide, whereas formyl hydroperoxide hydrolyses rapidly. The latter reaction can conveniently be followed polarographically.

Using lanthanum acetate in alkaline solution, acyl hydroperoxides are precipitated as hydrogen peroxide. A slight loss of peroxide in the form of molecular oxygen occurs.

It may be mentioned that the corresponding carboxylic acids are not active polarographically except for the H^+ — ions.

MIXTURES OF PEROXIDES

In the homologuous series of alkyl hydroperoxides, it is not possible to separate the polarograms of adjacent members. However, comparison of the polarogram of a mixture of peroxides with polarograms of the pure substances shows that the polarograms, and in particular the limiting diffusion currents, are additive. Alkyl peroxides differing by two carbon atoms, *e.g.* H_2O_2 and EtOOH, or MeOOH and *tert.*-BuOOH, can be distinguished by the different position of their steps. The separation can often be extended by using alkaline solutions (see Table I).

As a result of the present work, two methods have become available for estimating hydrogen peroxide in the presence of alkyl peroxides. In alkaline solution, the concentration of hydrogen peroxide is determined directly from the anodic step ($E_{1/2}$ = —0.1 volts), while that of the total peroxides is determined from the limiting diffusion current at —1.6 volts (Fig. 6).

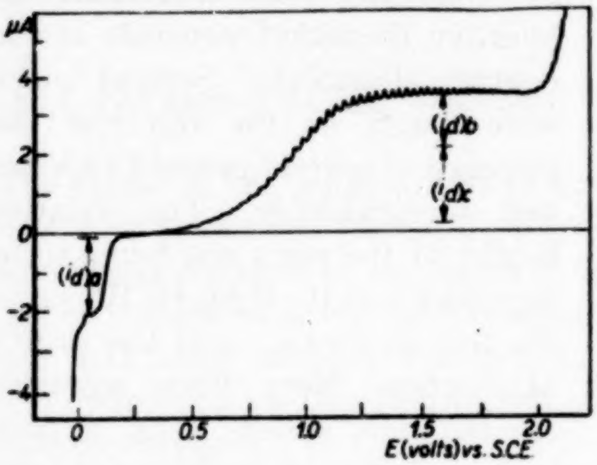


Fig. 6. Polarogram of a mixture of hydrogen peroxide (0.36m*M*) and methyl hydroperoxide (0.31m*M*).
Electrolyte: 0.1*M* Li_2SO_4, 0.01*M* LiOH
$(i_d)_a = —(id)c$: corresponds to HOOH
(i_d):$_b$ corresponds to CH_3OOH

If the concentration of hydrogen peroxide is high compared to that of the alkyl peroxides, all the hydrogen peroxide can be precipitated in alkaline solutions with lanthanum acetate, leaving in solution only the alkyl peroxides whose polarograms can then be obtained without interference.

Although the lanthanum precipitate caused a slight decomposition of the alkyl peroxides, it was possible to analyse these peroxides when their concentration was as low as one per cent of that of the hydrogen peroxide.

When acyl hydroperoxides are also present, it is necessary to run two polarograms, one in acid solution, and another in alkaline solution after the addition of the lanthanum. For quantitative analysis, a correction must be applied for the change in *D'* on passing from acid solutions (in which *D'* has the same value as in neutral solutions) to alkaline media.

Using these methods, it is possible to estimate separately the concentrations in a mixture of hydrogen peroxide, methyl-, *tert.* butyl- and acyl hydroperoxides, and diethyl peroxide.

DETERMINATION OF PEROXIDES IN THE PRESENCE OF ALDEHYDES

The effect of aldehydes on the polarographic determination of peroxides has been investigated, since aldehydes are usually present in combustion products.

Hydrogen peroxide and formaldehyde

In neutral or acid solutions these two compounds react reversibly to form hydroxy alkyl peroxides (RIECHE[10], DUNICZ, PERRIN AND STYLE[11], KOOIJMAN AND GHIJSEN[12]):

$$HOOH + HCHO \rightleftharpoons HCH(OH)OOH$$

$$HCH(OH)OOH + HCHO \rightleftharpoons HCH(OH)OO(OH)HCH$$

References p. 200.

Fig. 7 shows the polarogram obtained after dilution of an aqueous solution of 2 moles/l of hydrogen peroxide and 4 moles/l of formaldehyde which had been allowed to stand for 24 hours at room temperature.

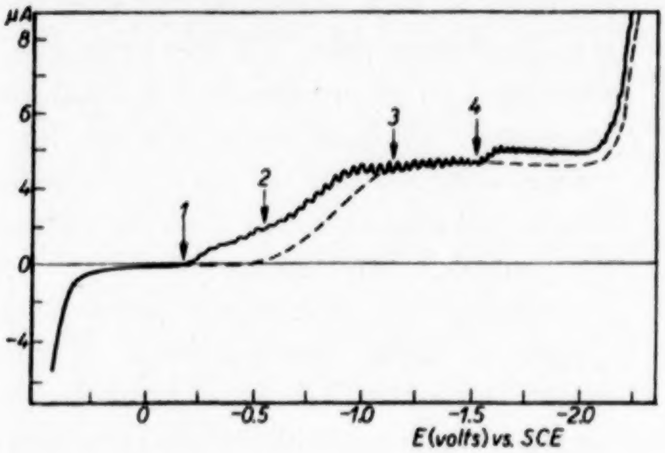


Fig. 7. Polarogram of a mixture of hydrogen peroxide and formaldehyde. Electrolyte: to.1M Li_2SO_4
- - - hydrogen peroxide alone
description: see text.

Similar polarograms were obtained by dissolving pure crystalline dihydroxy di-methyl peroxide in the neutral electrolyte. Several steps were found, as the result of the presence of several peroxidic species and formaldehyde. The relative height of the steps was found to be dependent on the H_2O_2/HCHO ratio, the time of contact and the degree of dilution. More dilute solutions reacted more slowly; thus, a decimolar solution of hydrogen peroxide and formaldehyde showed, after 5 hours, only a slight shift to more positive potentials.

The diffusion current (at −1.6 V) of the concentrated solution decreased slightly, but was still within 5% of that of the same concentration of pure hydrogen peroxide. Hydrogen peroxide can thus be determined quantitatively in the presence of formaldehyde in neutral or acid solutions.

In the alkaline electrolyte, considerable destruction of the peroxide was observed, so that the anodic step was no longer a measure of the original peroxide concentration. The estimation of hydrogen peroxide could still be carried out, however, by determining the difference between the cathodic diffusion current in acid or neutral solution and the cathodic diffusion current in alkaline solution after the addition of the lanthanum reagent.

Higher members

Approximately decimolar solutions of hydrogen peroxide and acetaldehyde, and of methyl- and ethyl hydroperoxide with formaldehyde and acetaldehyde, were allowed to stand for 24 hours at room temperature. At the end of this time, polarograms in the neutral electrolyte showed no change in reduction potential, as compared with that of the pure peroxide, and a decrease of less than 3% in the diffusion current.

When the same mixtures were made up and examined with the polarograph in the alkaline electrolyte, no evidence was obtained of any reactions. Even when a mixture of acetaldehyde and ethyl hydroperoxide was left in the polarographic cell for 2 hours in stronger alkali (0.1N) than is normally used, the diffusion current did not decrease by more than 5%.

The absence of any polarograms of the addition compounds (NORRISH AND KNOX[13]) in the hydrogen peroxide acetaldehyde system is surprising, since both the equilibrium constants and the initial rates of the formation of hydroxy ethyl peroxides in water have been reported (KOOIJMAN AND GHIJSEN[12], SATTERFIELD AND CASE[14]). A further investigation of this problem is in progress.

Acyl hydroperoxides and aldehydes

The shape of the polarograms of acyl hydroperoxides is not affected by the presence of aldehydes. Identical polarograms were obtained when acetyl hydroperoxide was prepared by oxidation of liquid acetaldehyde with molecular oxygen. In aqueous solution, acetyl hydroperoxide and acetaldehyde react with each other, acetic acid being formed. The rate of this reaction was followed at 25.00° C, acetyl hydroperoxide being estimated at different times by the iodometric method described earlier.

Fig. 8 shows the effect on the rate of doubling the initial peroxide concentration (curves *A* and *B*, half scale), and the initial aldehyde concentration (curves *A* and *C*). The initial rates have the ratio $A : B : C = 1.0 : 1.9 : 2.6$. Fig. 9 shows the rate of reaction in acid and in alkaline solutions. The reaction is clearly strongly base catalysed, and is slightly inhibited by acids.

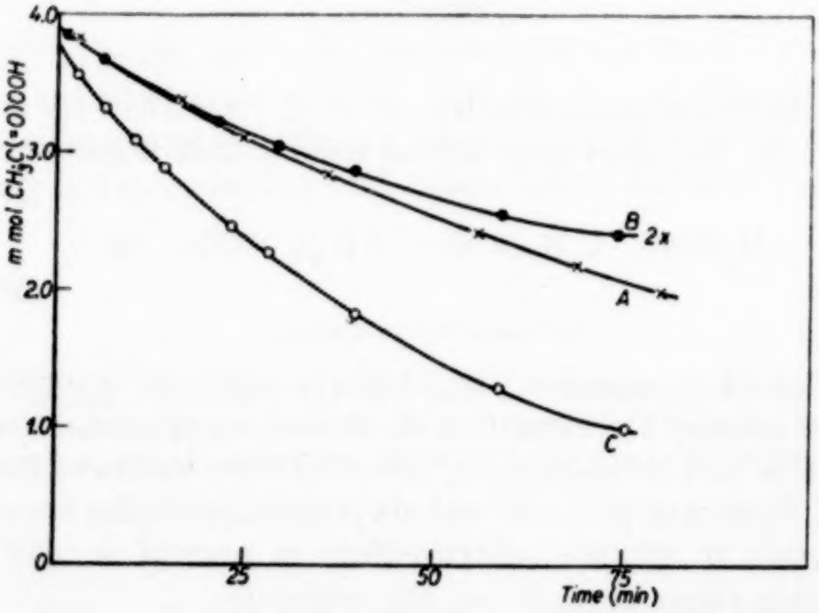


Fig. 8. Reaction of acetyl hydroperoxide with acetaldehyde. Effect of initial concentration.
$A = 0.010M$ $CH_3CHO + 0.00394M$ $CH_3.CO.OOH$
$B = 0.010M$ $CH_3CHO + 0.00788M$ $CH_3.CO.OOH$
$C = 0.020M$ $CH_3CHO + 0.00394M$ $CH_3.CO.OOH$

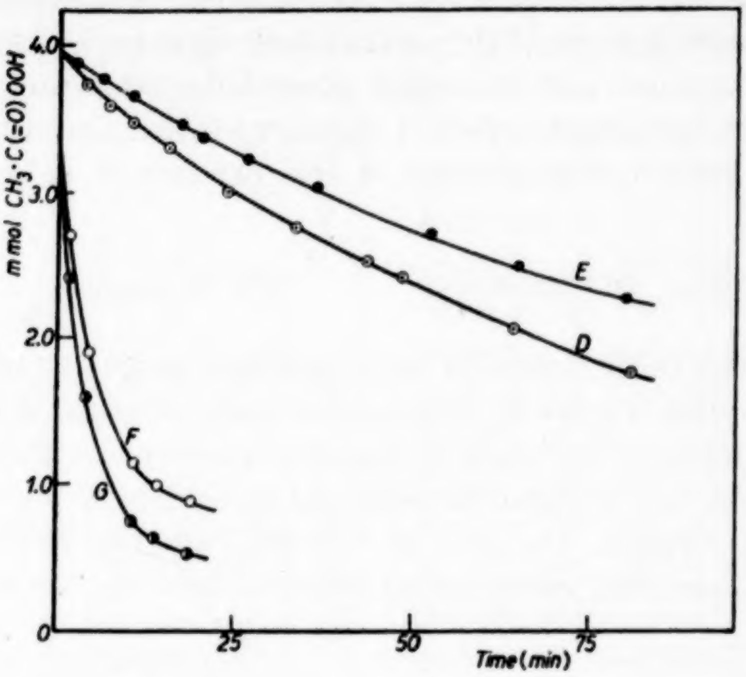
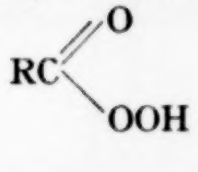


Fig. 9. Reaction of acetyl hydroperoxide with acetaldehyde. Effect of addition of acid and of alkali.
D = 0.0102M CH_3CHO + 0.00394M $CH_3CO.OOH$
E = same + 0.010M H_2SO_4
F,G = same + 0.010M NaOH

DISCUSSION

The cathodic halfwave potentials depend on the nature of the radical attached to the –OO– group. The order observed on passing from negative to more positive potentials is:



$$HOOH,\ CH_3OOH,\ C_2H_5OOH,\ (CH_3)_3COOH,\ RC{\overset{O}{\Large\nearrow}} \atop {\searrow OOH}$$

In the series of alkyl peroxides, the halfwave potential becomes more positive with larger alkyl groups. The formation of addition compounds, observed between hydrogen peroxide and formaldehyde, also shifts the halfwave potential to more positive values. Hydrogen peroxide and alkyl hydroperoxides are reduced at more negative potentials in alkaline solution than in neutral or acid solutions. The magnitude of this effect depends on the molecule.

According to KOLTHOFF[15], the electrochemical reduction of hydrogen peroxide proceeds basically by a split of the O–O bond, with the acceptance of two electrons:

$$HOOH + 2\,e \rightarrow 2\,HO^-$$

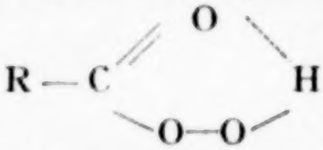
References p. 200.

The similarities in the polarographic behaviour of the alkyl hydroperoxides suggests that a similar mechanism may be effective:

$$ROOH + 2\,e \rightarrow RO^- + OH^-$$

At first sight, it seems tempting to use the above series to increase our knowledge of the strength of the peroxide bond, by relating the halfwave potentials of the peroxides to the energy changes of the electrode reaction. Owing to insufficient theoretical understanding of irreversible electrode reactions, however, no simple correlation is available at the present time (DELAHAY AND BERZINS[16]).

Finally, the relative diffusion rates will be discussed. If the assumption is made that the number of electrons involved in the cathodic reduction is the same for all peroxides, then since $D'_x = \frac{\sqrt{D_x}}{\sqrt{D_{H_2O_2}}}$ the D' values in Table I indicate the rates of diffusion relative to that of hydrogen peroxide. It is clear from these figures that the rates of diffusion depend not only on the formal molecular weight, but also on the strength of the interaction with the solvent. Thus diethyl peroxide, which is unhydrated, diffuses at approximately the same rate as ethyl hydroperoxide. By contrast, acyl hydroperoxides appear to diffuse more rapidly than does hydrogen peroxide. This could be explained if the former were chelated.



This type of chelation has been suggested by GIGUÈRE AND OLMOS[17] as the results of infra-red absorption studies, both in the gas phase and in non-polar solvents. The intramolecular hydrogen bond would involve less interaction with the surrounding water molecules and hence larger diffusion rates.

ACKNOWLEDGEMENTS

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SUMMARY

Some lower alkyl and acyl hydroperoxides and dialkyl peroxides have been prepared and their i_d/c values and halfwave potentials have been determined. The halfwave potentials become successively less negative on passing from hydrogen peroxide up the series, the order being

H_2O_2, CH_3OOH, EtOOH, $(CH_3)_3COOH$, R-CO(OOH)

The limiting diffusion currents have been shown to be proportional to the concentrations of individual peroxides, and to be additive in mixtures. Methods have been developed which permit the detailed analysis of mixtures of peroxides containing, for example, hydrogen peroxide, methyl-, *tert.*-butyl and acetyl hydroperoxides, and diethyl peroxide. The effect of aldehydes has been investigated.

RÉSUMÉ

Quelques hydroperoxydes inférieurs d'alcoyle, d'acyle et de dialcoyle ont été préparés; leur valeur de i_d/c et leur potentiel de demi-vague ont été déterminés. Les potentiels $E_{1/2}$ deviennent de plus en plus négatifs lorsqu'on passe du peroxyde d'hydrogène aux peroxydes supérieurs, dans l'ordre suivant par exemple:

H_2O_2, CH_3OOH, C_2H_5OOH, $(CH_3)_3COOH$, R-CO(OOH)

Les courants de diffusion sont proportionnels aux concentrations des peroxydes. Des méthodes ont été établies permettant le dosage simultané d'un mélange de peroxydes, renfermant par exemple: peroxyde d'hydrogène, hydroperoxydes de méthyle, de *tert.*-butyle et d'acétyle, et de peroxyde de diéthyle. L'influence des aldéhydes a été examinée.

ZUSAMMENFASSUNG

Einige niederige Alkyl- und Acylhydroperoxyde, sowie Dialkylperoxyde wurden dargestellt; ihr Wert für i_d/c und ihr Halbwertspotential wurden bestimmt. Die Potentiale $E_{1/2}$ werden immer mehr nach der negativen Seite verschoben, wenn man vom Wasserstoffperoxyd zu den höheren Peroxyden übergeht, zum Beispiel in der folgenden Reihe:

H_2O_2, CH_3OOH, C_2H_5OOH, $(CH_3)_3COOH$, R-CO(OOH)

Die Diffusionsströme sind den Konzentrationen an Peroxyden proportional. Es wurden Methoden gefunden, welche eine gleichzeitige Bestimmung eines Gemisches verschiedener Peroxyde ermöglicht; zum Beispiel eines Gemisches von Wasserstoffperoxyd, Methylhydroperoxyd, *tert.*-Butyl und Acetyl und Diethylperoxyd. Der Einfluss der Aldehyde wurde geprüft.

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5-METHYL-7-NITROSO-8-HYDROXYQUINOLINE AND ITS SENSITIVITY AND SELECTIVITY TOWARDS CERTAIN METALLIC IONS

by

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INTRODUCTION

5-Methyl-oxine, first prepared by NÖLTING AND TRAUTMANN[1] has been investigated as a potential analytical reagent for the detection of certain metals by GIETZ AND SÁ[2]. These authors described the detection of ferric iron, copper, cobalt, nickel, palladium, titanium, zinc, cadmium, magnesium, vanadium (as vanadate) and tungsten (as tungstate). SÁ[3] described its use for the identification and determination of palladium.

As other substituted oxines containing a nitroso group have been investigated as possible analytical reagents, it appeared to be of interest to investigate the effect, if any, that the introduction of a nitroso group would have in position 7 in 5-methyl-oxine. It is known that 5-nitroso-oxine is far more selective in its action[4] than is 2-methyl-5-nitroso-oxine[5]. Neither of these reagents chelate with certain members of Group III B metals. The possibility of steric hindrance in the case of the 2-methyl-5-nitroso-derivative, and the increased acidity arising from the presence of the nitroso group in position 5, may largely be responsible for these results. In 5-methyl-7-nitroso-oxine, the steric effect would be absent, but the acidity due to the nitroso group is retained. It was, therefore, considered to be of interest to investigate its behaviour towards certain metals.

Sensitivity and selectivity tests

The method based on that suggested by LUTZ[6] and used by IRVING *et al.*[7] and HOLLINGSHEAD[8] was employed. This consists essentially in recording the sensitivity in terms of the smallest amount of metal which will give a perceptible precipitate in a test solution under standard conditions.

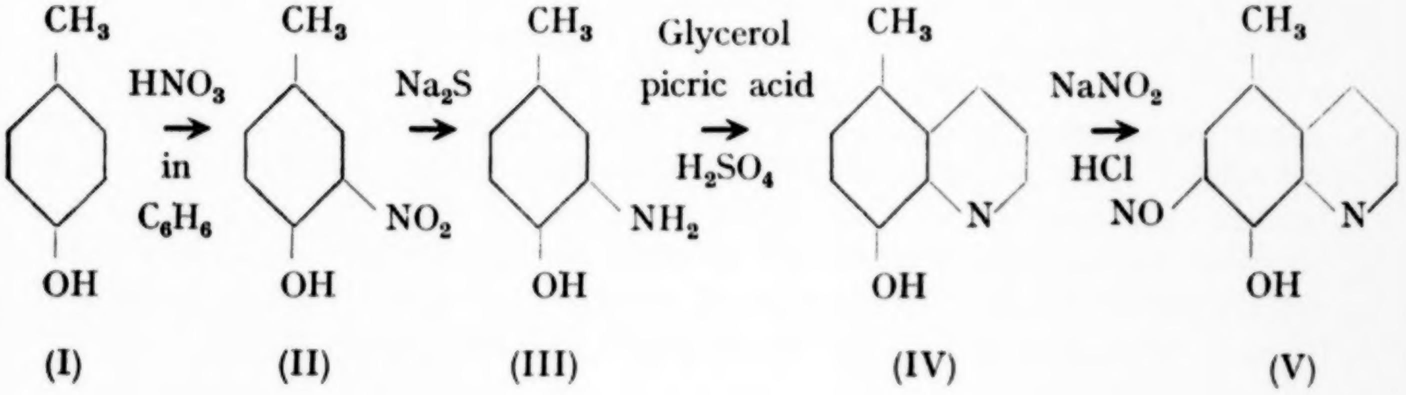
Three buffer solutions, A, B and C, having pH's of 5.3, 8.35 and 13.1 respectively, were prepared in bulk from AnalaR reagents. For each test the total volume of solution was 7 ml and the reagent solution was 0.02*M* in absolute ethyl alcohol. Decreasing amounts of metal were used in successive tests until the absolute limit of detection of precipitate formation was obtained. The results obtained are expressed as volumes of standard metal solutions which (a) gave a perceptible precipitate (V_1) and (b) failed to give a precipitate (V_2). The larger volume (V_1) was taken as a conservative estimate of the sensitivity.

The expression pL has been employed by IRVING[7] and is used here. This is defined as $-\log_{10}$ limiting concentration, in gram equivalents per litre, for the volumes V_1 and V_2 respectively. This value is preferred as an expression of sensitivity, as the use of µg per ml as usually employed may convey a false impression of the difference in sensitivities of the reagent with various metals of differing atomic weight or valency. This is to some extent corrected by the use of pL.

EXPERIMENTAL

Preparation of 5-methyl-7-nitroso-oxine

NÖLTING AND TRAUTMANN[1] described the preparation of 5-methyloxine (IV) by means of a Skraup reaction on 3-amino-*p*-cresol (III), obtaining the desired product in 65 per cent yield. Modifications to this method of preparation and the preparation of the 3-amino-*p*-cresol required have been made. 5-Methyl-7-nitroso-oxine was, therefore, prepared by the following route:



*Preparation of 3-nitro-*p*-cresol (II)*

This was prepared in good yield by nitration of *p*-cresol[9]. The nitration was carried out in benzene solution.

*Conversion of 3-nitro-*p*-cresol to 3-amino-*p*-cresol (III)*

A facile method of conversion to the amino compound was found to be that suggested by ASCHKINAZI AND RABONOVITSH[10] using sodium sulphide. The amino compound was precipitated by the addition of sodium bisulphite:

114 g	sodium sulphide hydrated
1200 ml	distilled water
55 g	3-nitro-*p*-cresol

The sodium sulphide is dissolved in the water and the solution filtered. The sulphide solution is transferred to a 3 litre round-bottomed flask on an electric mantle, and heated to boiling. The 3-nitro-*p*-cresol is added in small portions to the boiling sulphide solution to give a deep red liquid. After the careful addition of all the 3-nitro-*p*-cresol, the flask is fitted with a reflux condenser and the mixture refluxed for 5 hours. After cooling, a further 114 g of sodium sulphide, dissolved in 1 litre of water, is added and the reflux resumed for a further 5 hours, by which time the red colouration has disappeared. The mixture is allowed to cool to 55° C and then a solution of sodium bisulphite, prepared by saturating sodium carbonate solution with sulphur dioxide, added slowly, with stirring, to precipitate the 3-amino-*p*-cresol as off-white lustrous plates. The precipitated amino-cresol is allowed to stand until the mixture is at room temperature, removed, using a sintered glass filter, porosity No. 3, washed with a little water and pressed as dry as possible *in situ*. (Yield of crude material = 49 g). The crude material is purified by a double recrystallization from boiling ethyl alcohol, M.Pt = 134.9° C (NÖLTING[11] gives 135° C).

*Conversion of 3-amino-*p*-cresol to 5-methyl-oxine (IV)*

10 g	3-amino-*p*-cresol
24 g	glycerol
2 g	picric acid
20 g	sulphuric acid concentrated

The glycerol is dried by heating to 180° C for 40 min and cooled in a desiccator. The dry amino cresol and picric acid are intimately mixed in a 2 litre round-bottomed flask and the glycerol added and mixed thoroughly. The sulphuric acid is added in small portions with shaking after each addition, the flask fitted with a wide air condenser and the flask and contents heated gently on a sand bath. After the initial vigorous reaction is completed the flask and contents are heated at reflux temperature on the sand bath for 4 hours. After cooling completely, 400 ml of water is added cautiously and the whole shaken and stirred to break up the resinous mass. The mixture is made just alkaline by the addition of 10N sodium hydroxide solution, and then strongly acidified by the addition of glacial acetic acid. The contents of the flask are then steam distilled to give a lime green distillate. The distillate, after cooling, is neutralized with 5N ammonium hydroxide until just alkaline, when 5-methyl-oxine precipitates as an off-white powder. This is removed at the pump, using sintered glass porosity No. 3, washed *in situ* with a small quantity of water and dried at 50° C *in vacuo*. Yield of crude, yellowish white material = 10.2 g.

A sample was recrystallized three times from ethyl alcohol to give a white crystalline material, M.Pt. 123° C. Analysis $C_{10}H_9ON$

Requires: —	C 75.45 %;	H 5.7 %;	N 8.8 %
Found: —	C 74.83 %;	H 6.4 %;	N 8.65 %

Nitrosation of 5-methyl-oxine

5.3 g	5-methyl-oxine
7 ml	hydrochloric acid, concentrated
2.3 g	sodium nitrite

The 5-methyl-oxine is dissolved in a mixture of 7 ml of concentrated hydrochloric acid and 30 ml of water. To the stirred solution is added a solution of 2.3 g of sodium nitrite, dissolved in the least possible amount of water. After stirring for 30 minutes, precipitation of 5-methyl-7-nitroso-oxine hydrochloride begins. The mixture is stirred for a further hour, neutralized with sodium carbonate, stirred for a further hour and allowed to stand over-night. The free base is filtered at the pump, washed with a small amount of cold distilled water, dried as far as possible *in situ*, and recrystallized three times from boiling ethyl alcohol to give the pure base in 70 per cent yield. M.Pt. 210° C (w.d.).

Analysis gave:

Calculated	C 63.8%;	H 4.3%;	N 14.9%;
Found	C 64.0%;	H 4.38%;	N 14.95%.

TESTING OF REAGENT WITH METALS

Preparation of buffer solutions

These were prepared from AnalaR grade materials as follows:

Buffer A	250 ml	2*N* acetic acid	
	225 g	sodium acetate hydrated	pH 5.3
	500 ml	redistilled water	
Buffer B	40 ml	2*N* ammonium hydroxide	
	320 g	ammonium acetate	
	30 g	sodium potassium tartrate	pH 8.35
	850 ml	redistilled water	

Buffer C	500 ml	$2N$ sodium hydroxide	
	275 g	sodium potassium tartrate	pH 13.1
	500 ml	redistilled water	

The pH's of the above solutions were determined using a Doran pH meter, Model 4980, and a lithium glass "alk-acid" electrode assembly through the range 0-14.

Preparation of metal solutions

Standard solutions of the metals were prepared from AnalaR grade materials wherever possible. When AnalaR grade materials were not available the purest material obtainable was taken and twice recrystallized before use. With gallium, a standard solution was prepared from the metal (99.999% Ga).

Preparation of reagent solution

The reagent solution was $0.02M$ in absolute ethyl alcohol. Although solvent effect mitigates against the use of alcoholic solutions of oxine derivatives giving a high alcohol concentration in the final solution, the low solubility of certain of these derivatives necessitates the use of a comparatively dilute solution, so that standardization of concentrations and volumes may be attained throughout a series of investigations into the sensitivity of oxine derivatives.

Procedure for testing of reagent

4.0, 0.4 and 0.04 ml of $0.01M$ metal solution were placed severally in three test tubes (5 × 5/8 previously boiled in nitric acid and repeatedly washed in redistilled water and finally steamed with live steam from boiling redistilled water). 2 ml of Buffer A, 1 ml of the reagent solution and sufficient redistilled water to bring the volume up to 7 ml were then added. A fourth tube contained 2 ml of buffer, 1 ml of reagent solution and 4 ml of water and served to determine the behaviour of the reagent, and a further tube containing 0.4 ml of metal solution, 2 ml of buffer and 4.6 ml of water with no reagent, ensured that the possible precipitation of metal as hydroxide could not be mistaken for complex formation under the conditions of the test. Each tube was heated in a water bath at 80° C for 15 min, removed, and allowed to cool completely before examination. If a positive result was obtained with the tube containing 0.04 ml of $0.01M$ metal solution, the whole series was repeated with $0.001M$ metal solution, and, if necessary, with $0.0001M$ metal solution, until precipitation did not take place.

The sensitivity limits were then determined with greater accuracy by taking 0.4, 0.2, 0.1 and 0.04 ml of the metal solution of the appropriate strength. This procedure was repeated with buffers B and C.

The results obtained for buffers A, B and C are given in Tables I, II and III respectively.

TABLE I

	Buffer A	pH = 5.3		Total volume = 7 ml
Metal	Molarity *M*	V_1 — V_2 mls	pL	Colour of precipitate
Al^{+3}	10^{-3}	0.1—0.04	4.84—5.24	Yellow
Cd^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Yellow
Ce^{+3}	10^{-2}	0.4—0.04	3.24—4.24	Chocolate (a); yellow (b).
Ce^{+4}	10^{-3}	0.3—0.2	4.37—4.54	Orange brown
Cr^{+2}	10^{-3}	0.4—0.3	4.24—4.37	Orange
Co^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Yellow
Cu^{+2}	10^{-2}	0.4—0.04	3.24—4.24	Greenish-yellow
Fe^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Green
Fe^{+3}	10^{-3}	0.1—0.04	4.84—5.24	Green
Ga^{+3}	10^{-3}	0.1—0.04	4.84—5.24	Yellow
Pb^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Yellow
Mg^{+2}	10^{-3}	0.4—0.3	4.24—4.37	Yellow
Hg^{+}	10^{-3}	0.2—0.1	4.54—4.84	Orange
Hg^{+2}	10^{-4}	0.2—0.1	5.54—5.84	Red (a); Yellow (b).
Ni^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Yellow (a); Orange (b)
Tl^{+}	10^{-3}	0.4—0.3	4.24—4.37	Orange
VO_3^{-2}	10^{-3}	0.1—0.04	4.84—5.24	Brown (a); Orange-yellow (b)
Zn^{+2}	10^{-4}	0.3—0.2	5.37—5.54	Yellow

(a) at high concentrations; (b) at low concentrations.

TABLE II

	Buffer B	pH = 8.35		Total volume = 7 ml
Metal	Molarity *M*	V_1 — V_2 ml	pL	Colour of precipitate
Al^{+3}	10^{-2}	0.4—0.04	3.24—4.24	Yellow
Cd^{+2}	10^{-3}	0.2—0.1	4.54—4.84	Yellow
Ce^{+3}		Metal precipitates	out	
Ce^{+4}		Metal precipitates	out	
Cr^{+2}	10^{-2}	0.4—0.04	3.24—4.24	Yellow-orange
Co^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Orange-yellow
Cu^{+2}	10^{-2}	0.4—0.04	3.24—4.24	Greenish-yellow
Fe^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Yellow
Fe^{+3}	10^{-3}	0.1—0.04	4.84—5.24	Green
Ga^{+3}	10^{-3}	0.1—0.04	4.84—5.24	Yellow fluorescent
Pb^{+2}		Metal precipitates	out	
Mg^{+2}	10^{-2}	0.4—0.04	3.24—4.24	Yellow
Hg^{+}		Metal precipitates	out	
Hg^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Orange
Ni^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Yellow green
Tl^{+}	10^{-3}	0.4—0.3	4.24—4.37	Orange
VO_3^{-2}	10^{-2}	0.4—0.04	3.24—4.24	Brown (a); Yellow (b)
Zn^{+2}	10^{-3}	0.1—0.04	4.84—5.24	Yellow fluorescent

(a) at high concentrations; (b) at low concentrations.

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TABLE III

	Buffer C		pH = 13.1	Total volume = 7 ml
Metal	Molarity M	V_1 — V_2 ml	pL	Colour of precipitate
Al^{+3}		N.P.*		
Cd^{+2}		Metal precipitates out		
Ce^{+3}	10^{-2}	0.4—0.04	3.24—4.24	Orange
Ce^{+4}	10^{-2}	4.0—0.4	2.24—3.24	Orange
Cr^{+2}		Indefinite and unreliable		
Co^{+2}		Indefinite and unreliable		
Cu^{+2}	10^{-2}	4.0—0.4	2.24—3.24	Olive green
Fe^{+2}		N.P.		
Fe^{+3}		N.P.		
Ga^{+3}		N.P.		
Pb^{+2}		N.P.		
Mg^{+2}	10^{-2}	0.4—0.04	3.24—4.24	Yellow
Hg^{+}		Metal precipitates out		
Hg^{+2}		Metal precipitates out		
Ni^{+2}	10^{-3}	0.1 — 0.04	4.84—5.24	Yellow (a); orange (b)
Tl^{+}	10^{-2}	0.4—0.04	3.24—4.24	Orange yellow
VO$_3^{-2}$		N.P.		
Zn^{+2}		Metal precipitates out		

N.P. = no precipitate
* The reagent prevents precipitation of metal at this pH;
(a) at high concentrations; (b) at low concentrations

DISCUSSION

It is apparent that the sensitivity, as defined by the term pL, remains remarkably constant through the range of metals investigated, with the exception of mercuric mercury. IRVING[7] notes that it is surprising to find that the individual variations of sensitivity among such oxine derivatives as 2-methyl, 5-methyl, 6-methyl, and 7-methyl, are indeed small when compared with an average pL value which he gives as 4.2. Taking this pL value, IRVING *et al.* remark on the rather superior average sensitivity of 7-methyl-oxine towards the metals investigated, namely, aluminium, chromium, ferric iron, copper, zinc, and gallium. This superior sensitivity was attributed to a steric effect, as the introduction of the methyl group in positions 5 and 6 only produced a relatively small increase in sensitivity.

Although the average sensitivity of 5-methyl-7-nitroso-oxine is somewhat greater than that of the parent compound, its selectivity is comparable with that of oxine, in that chelation occurs with all the metals used in this investigation.

A great increase in selectivity is obtained by the introduction of a nitroso group in position 5 but at the same time the sensitivity is lowered considerably[12]. 5-Nitroso-oxine does not chelate with aluminium, yttrium, gallium and indium, and under the conditions of the test, only with difficulty with trivalent thallium[5].

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This failure to give precipitates with the above metals may possibly be explained by the fact that the reagent has an increased acidity over that of oxine (pK values are 2.8 and 7.17 as compared with 5.0 and 9.8 for oxine)[4].

When a methyl group is introduced in position 2 with a nitroso group maintained at position 5 the probability of steric hindrance arises and together with the increased acidity, results in non-chelation with aluminium, yttrium, gallium, indium and trivalent thallium under the conditions of the test[5]. When the methyl group is in position 5 and the nitroso group in position 7 there is a reversion in the selectivity and an increase in the sensitivity, and chelation occurs with the above metals.

As 5-methyl-7-nitroso-oxine is more basic than 5-nitroso-oxine this behaviour might be expected. It would be of interest to examine the effects of substitution of methyl and nitroso groups at other positions in the oxine molecule in order to correlate structure with behaviour in a series of oxine derivatives.

A comparison of the results obtained here with those obtained by GIETZ AND SÁ for 5-methyl-oxine[2] is not possible, as these authors give no information regarding the pH of precipitation with the metals investigated.

Some comparison may, however, be made with the pL values given by IRVING *et al.*[7] These are given in Table IV.

TABLE IV

	Al^{+3}	Cr^{+3}	Fe^{+3}	Cu^{+2}	Zn^{+2}	Ga^{+3}
5-Methyl-oxine *	4.0	4.0	4.3	4.5	3.5	4.0
5-Methyl-7-nitroso-oxine **	4.8	4.2	4.8	3.2	5.4	4.8

* Given for the medium in which the greatest sensitivity was shown.
** Values obtained in buffer A from Volume V_1.

The above figures show that there is an increase in the sensitivity with 5-methyl-7-nitroso-oxine and aluminium, chromium, gallium, iron and zinc, but there is a surprising reversal of sensitivities in the case of copper. The value of 3.2 for copper with 5-methyl-7-nitroso-oxine may also be compared with IRVING *et al.* value of 5.3 for 7-methyl-oxine. This low sensitivity cannot be attributed in this case to the presence of the nitroso group as, although 5-nitroso-oxine has a low sensitivity with most metals[12] it is remarkable that with copper in buffer A, and also buffer B, this reagent shows its maximum sensitivity in the range of metals examined, the pL value being 5.0. Further investigation is necessary to elucidate this point.

5-Methyl-7-nitroso-oxine shows its greatest sensitivity towards divalent mercury at a pH of 5.3, the pL value, 5.5, being remarkably high, when compared with the average pL value given by IRVING *et al.* This corresponds to a limiting sensitivity of between 0.6 and 0.3 µg/per ml. This reagent may, therefore, have some application for the detection of traces of divalent mercury, although its extreme "unselectivity" will mitigate against its use analytically to any great extent.

From Table III it may be seen that with aluminium, iron^{+2}, iron^{+3} gallium^{+3}, lead^{+2} and vanadium (as vanadate) no precipitation occurs.

IRVING *et al.* have noted this behaviour[7] with aluminium and oxine, and consider it due to the formation of salts of complexions with the reagent such as $[Al(H_2O)_2Ox_2]^+$, $[Al(H_2O)_4Ox]^{+2}$ or $[Al(OH)_2Ox_2]^-$, etc. It would appear that a similar behaviour might account for the non-precipitation described above.

It is of interest to note that with cadmium^{+2}, mercury^{+}, mercury^{+2} and zinc, the metal precipitates out at pH 13.1 in the presence of the reagent. Why the reagent does not hold up the Group II B metals is not clear at present, and with the meagre evidence available no satisfactory theory may be advanced. Doubtless further investigation will elucidate this problem.

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SUMMARY

5-Methyl-7-nitroso-8-hydroxyquinoline (5-methyl-7-nitroso-oxine), hitherto undescribed, has been prepared and tested for its sensitivity and selectivity towards various metallic ions at differing pH's. The metals tested include cadmium, ferrous and ferric iron, mercurous and mercuric mercury, lead, nickel, cobalt, thallous thallium, cerous and ceric cerium, copper, chromium, aluminium, zinc, magnesium, vanadium (as vanadate) and gallium. This reagent is comparatively "unselective" in that it chelates with all the above metals under the conditions employed, and therefore closely follows the behaviour of the parent compound, 8-hydroxyquinoline (oxine). Its average sensitivity is somewhat greater than that of the parent compound, and it shows its greatest sensitivity with divalent mercury.

RÉSUMÉ

La 5-méthyl-7-nitroso-8-hydroxyquinoléine (5-méthyl-7-nitroso-oxine) non encore décrite, a été préparée et étudiée pour l'identification de plusieurs ions métalliques. L'auteur a examiné la sensibilité et la spécificité des réactions obtenues à différents pH, avec le cadmium, le fer(II), le fer(III), le mercure(I), le mercure(II), le plomb, le nickel, le cobalt, le thallium(I), le cérium(III), le cérium(IV), le cuivre, le chrome, l'aluminium, le zinc, le magnésium, le vanadium (comme vanadate) et le gallium. Ce réactif n'est pas spécifique, il donne des chélates avec tous les éléments mentionnés ci-dessus, dans les conditions utilisées, se comportant comme la 8-hydroxyquinoléine (oxine). Sa sensibilité moyenne est cependant meilleure que celle de l'oxine. C'est avec le mercure(II) que la sensibilité est la plus grande.

ZUSAMMENFASSUNG

Das 5-Methyl-7-nitroso-8-oxychinolin (5-Methyl-7-nitroso-oxin), welches bisher noch nicht beschrieben worden ist, wird dargestellt und im Hinblick auf den Nachweis von mehreren Metallionen untersucht. Der Autor hat die Empfindlichkeit und die Spezifität geprüft von den erhaltenen Reaktionen bei verschiedenen pH-Werten mit Kadmium, Eisen(II), Eisen(III), Quecksilber(I), Quecksilber(II), Blei, Nickel, Kobalt, Thallium(I), Cerium(III), Cerium(IV), Kupfer, Chrom, Aluminium, Zink, Magnesium, Vanadium (als Vanadat) und Gallium. Dieses Reaktiv ist nicht spezifisch. Es gibt unter den angewandten Bedingungen mit allen obgenannten Elementen Chelate und verhält sich wie das 8-Oxychinolin (Oxin). Seine durchschnittliche Sensibilität ist indessen besser als diejenige des Oxins. Mit Quecksilber-(II) ist die Sensibilität am grössten.

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ISOPOLY-MOLYBDIC ACIDS

by

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INTRODUCTION

Molybdic acid has an enormous power of condensation, not only with itself but with a variety of other acids. The free molybdic acid, $H_2[MoO_4]\cdot H_2O$, appears as yellow crystals, separating slowly from a solution of a molybdate in conc. HNO_3. The yellow deposit often seen in bottles of ammonium molybdate solution for analytical work consists of this acid. According to AUGER[1] this deposit usually contains NH_3, and owes its yellow colour to traces of silicomolybdate from the glass. He finds[2] however that there is a brownish yellow labile form of H_2MoO_4. The viscosity of a colloidal solution of molybdic acid was measured by many workers[3]. From the measurements of conductivity, diffusion coefficient, *etc.*, JANDER indicated[4] the presence of several isopoly-anions of molybdenum under different pH conditions. It was shown[5] that conditions, favourable for isopoly acid formation, are not favourable for complex formation.

The difficulty about these polymers lies in the virtual impossibility of proving or disproving any theory one may put forward with the information available. Ionisation of the polymer as well as that of the added mineral acid (to vary the pH) prevents definite conclusions as to the molecular weight from conductivity, boiling and freezing points viscosity measurements, *etc.* Thus much uncertainty exists in the field of these molybdic acids, since all these studies deal with solutions only. It is of interest, therefore, to isolate some isopoly-molybdic acids in the solid state.

EXPERIMENTAL

Since these molybdic acids were shown earlier to be colloidal in nature, either heating in a sealed tube or ageing for a very long time should result in the separation of a solid. Nearly 100 ml of 5% ammonium molybdate solution were taken in Pyrex two-litre conical flasks and nearly 2000 ml of buffer solutions having pH 4.6

and 2 were added. The resulting solutions were allowed to stand for a number of days. After 40 days some solid began to separate and after 60 days an appreciable amount separated out. The pH of the supernatant liquid in contact with the solid was measured with a Marconi pH meter and found to be almost the same. Hence the solid is in equilibrium with solutions of these pH values. These were filtered, washed with the same buffers and a few ml of ether and were finally air dried. Any attempt to wash with water changes the composition of the solid, (as evidenced by the change in appearance and physical structure) owing to a change in pH to 7. The solid at pH 2 is light green in colour, shining and crystalline, and the solid at pH 4.6 is white and amorphous. These two have been heated and treated with a few drops of conc. HNO_3, if necessary, with the following results. All the quantitative experiments were repeated a number of times and the results were fairly concordant. Heating was done very cautiously since the oxide, MoO_3, sublimes at bright red heat[6].

RESULTS AND DISCUSSION

Solid at pH 2

Smell of ammonia is obtained, condensation of water particles and the mass turns bluish.

Solid at pH 4.6

No smell of ammonia is noticed, condensation of water particles and the mass remains almost unchanged.

Hence the first one appears to be an ammonium salt of the acid and the second a free acid. Broadly speaking, hexamolybdate ion is stable at pH 2 and trimolybdate ion at pH 4.6 according to JANDER. The following acids and ammonium acid salts are possible under the different conditions. The scheme of their decomposition on heating is represented below. When ammonia is evolved on heating it will reduce MoO_3 to a lower valent blue stage at that high temperature. In these cases a few drops of conc.HNO_3 are added and heated till the residue is white.

pH 4.6

Reaction	Approx. percentage loss on heating
1) $H_2MoO_4 \rightarrow H_2O + MoO_3$	12
2) $NH_4HMoO_4 \rightarrow NH_3 + H_2O + MoO_3$	20
3) $H_4Mo_3O_{11} \rightarrow 2H_2O + 3MoO_3$	7·7
4) $NH_4H_3Mo_3O_{11} \rightarrow 2H_2O + NH_3 + 3MoO_3$	11
5) $(NH_4)_2H_2Mo_3O_{11} \rightarrow 2H_2O + 2NH_3 + 3MoO_3$	14
6) $(NH_4)_3HMo_3O_{11} \rightarrow 2H_2O + 3NH_3 + 3MoO_3$	17

Actually the percentage loss on heating was found to be 7.66. This points to the third possibility of $H_4Mo_3O_{11}$. This appears to be sound since at this pH 4.6, trimolybdate ion exists in solution and further there is no ammonia smell on heating.

pH 2

Reaction	Approx. percentage loss on heating	
1) $H_6Mo_6O_{21} \rightarrow 3H_2O + 6\,MoO_3$	5.9	
2) $NH_4H_5Mo_6O_{21} \rightarrow NH_3 + 3H_2O + 6\,MoO_3$	7.6	
3) $(NH_4)_2H_4Mo_6O_{21} \rightarrow 2\,NH_3 + 3\,H_2O + 6\,MoO_3$	9.3	
4) $(NH_4)_3H_3Mo_6O_{21} \rightarrow 3\,NH_3 + 3\,H_2O + 6\,MoO_3$	10.9	↓

Actually, the percentage loss on heating and treating with conc. HNO_3 was found to be 7.83. This points to the second possibility of $NH_4H_5Mo_6O_{21}$. This appears to be sound since at this pH 2 hexamolybdate ion exists in solution and further there is a smell of ammonia on heating and the mass turns bluish. It can further be argued that as the aggregation process proceeds, the higher members of the series will be stronger acids than the lower members. Hence there is greater possibility for an acid salt to be precipitated than the free acid.

Thus one free molybdic acid and one ammonium acid molybdate could be isolated in the solid condition at pH 4.6 and 2 respectively and their compositions were explained according to JANDER's formulation in solution. It may be mentioned here that X-ray investigations indicate a Mo_7 unit instead of Mo_6 anion supposed by JANDER. According to that, the solid separated may be supposed to be $(NH_4)_2H_4Mo_7O_{24}$ where the percentage loss on heating corresponds to 8.03. Any conclusion on this point is reserved for a later investigation.

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SUMMARY

From the measurements of conductivity, diffusion coefficient *etc.*, JANDER indicated the presence of several isopoly-anions of molybdenum under different pH conditions. He and subsequent workers in the field dealt with solutions only. In the present work one free molybdic acid, and one ammonium acid molybdate were isolated in solid condition at pH 4.6 and 2. On analysis, their compositions were found to be $H_4Mo_3O_{11}$ and $NH_4H_5Mo_6O_{21}$ (or $(NH_4)_2H_4Mo_7O_{24}$) respectively.

RÉSUMÉ

En effectuant des mesures de conductivité, de coefficient de diffusion, *etc.*, JANDER a prouvé l'existence de plusieurs isopolyanions du molybdène à différents pH. Il a pu isoler un acide molybdique libre et un molybdate acide d'ammonium, aux pH 4.6 et 2, de composition $H_4Mo_3O_{11}$ et $NH_4H_5Mo_6O_{21}$ (ou $(NH_4)_2H_4Mo_7O_{24}$) respectivement.

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ZUSAMMENFASSUNG

Durch Messungen der elektrischen Leitfähigkeit, des Diffusionskoeffizienten usw. hat JANDER die Existenz mehrerer Isopolyanionen des Molybdäns bei verschiedenen pH-Werten nachgewiesen. Er konnte eine freie Molybdänsäure und ein saures Ammoniummolybdat isolieren bei pH-Werten von 4.6 und 2. Diese haben die folgenden Zusammensetzungen: $H_4Mo_3O_{11}$ und $NH_4H_5Mo_6O_{21}$ (oder $(NH_4)_2H_4Mo_7O_{24}$).

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LE DOSAGE INDIRECT DU MOLYBDÈNE PAR VOIE COMPLEXOMÉTRIQUE

par

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Nous avons déjà donné une méthode pour la séparation du molybdène et du tungstène, et pour le dosage de ce dernier, en utilisant le chlorure de calcium afin de précipiter ces deux métaux sous forme de molybdate et de tungstate de calcium[1,2]. La séparation est basée sur la solubilité du molybdate de calcium et sur la formation d'acide tungstique, insoluble dans l'acide chlorhydrique 1 : 1 à chaud.

Nous avons étudié une méthode indirecte pour la détermination du tungstène[3] en nous basant sur les propriétés du molybdate et du tungstate de calcium en présence d'acide chlorhydrique chaud. En effet, l'acide molybdique ne précipite pas, même en rendant le filtrat moins acide par addition de soude caustique ou d'ammoniaque. En milieu très alcalin et à chaud, le molybdate de calcium précipite quantitativement, une partie se déposant au fond du bécher et l'autre adhérant aux parois.

Comme le dosage par voie complexométrique, nécessite tout le calcium contenu dans le molybdate, pour le dosage indirect, comme dans le cas du tungstate de calcium, et que le calcium est dosé volumétriquement en milieu alcalin (pH 13), nous avons étudié un procédé permettant d'obtenir tout le calcium contenu dans le précipité de molybdate.

En effet, la solution contenant l'acide molybdique et le chlorure de calcium, après traitement par HCl, suivant la réaction $CaMoO_4 + 2HCl \rightarrow H_2MoO_4 + CaCl_2$ ne peut être utilisée directement pour le dosage du calcium. Nous l'avons alors évaporée à sec, chauffant la capsule au bain-marie pendant une heure, et après refroidissement, nous avons repris le résidu à l'aide d'eau chaude (à environ 50° C). Le chlorure de calcium se dissolvant ainsi, alors que l'acide molybdique reste insoluble. Par filtration tout le calcium reste et l'on peut le titrer par voie complexométrique. En multipliant le résultat par un facteur on obtient le pourcentage de molybdène.

TECHNIQUE

Le molybdène existe sous forme de molybdate de sodium, en solution. La concentration doit être environ 100 mg par 100 ml. Il faut avoir soin d'éliminer

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toute trace de tungstate, oxalate, sulfate et phosphate avant de procéder à la précipitation par une solution saturée de chlorure de calcium.

A la solution de molybdate de sodium, on ajoute à l'ébullition, 10 ml de solution saturée de chlorure de calcium par 100 mg de Mo^{+6}. On fait bouillir pendant quelques minutes et l'on refroidit le bécher en l'immergeant dans l'eau ou dans un bain glacé. Il est important de ne pas utiliser des béchers avec des rayures ou des défauts dans le propre verre, ainsi que des policemen en verre, car ceux-ci provoquent des centres de cristallisation du molybdate de calcium, difficiles à enlever lors des lavages.

Le précipité de molybdate de calcium, formé en présence d'un excès de solution saturée de chlorure de calcium, est quantitatif. Il s'agit de le filtrer en employant un papier Whatman No. 542 ou de type équivalent. Le précipité est lavé plusieurs fois (3 à 5) avec une solution 1 : 10 de chlorure de calcium, puis avec de l'eau bidistillée froide, 2 à 3 fois.

Ensuite on verse dans l'entonnoir de l'acide chlorhydrique 1 : 1 chaud (environ 50 à 60 degrés), jusqu'à dissoudre le molybdate de calcium dans le filtre. On lave 3 à 5 fois avec l'acide chlorhydrique 1 : 10 chaud. Le filtrat est ensuite évaporé à sec dans une capsule de porcelaine. La capsule est placée sur un bain de sable, et chauffée pendant une heure.

Après refroidissement le résidu est repris avec de l'eau chaude (environ 50°). On agite le contenu avec une baguette de verre et l'on filtre, lavant plusieurs fois la capsule et le filtre, avec de l'eau chaude. Si le volume du filtrat dépasse de beaucoup 200 ml, on l'évapore.

Le chlorure de calcium est prêt à être titré d'après la technique de SCHWARZENBACH et collaborateurs[4], avec une solution $0.1M$ de complexon III (sel disodique de l'acide éthylènediaminotétracétique). Suivant la teneur du calcium (que l'on peut évaluer par la quantité de précipité de molybdate de calcium), on utilise une burette de 50 ml ou une semi-micro-burette de 10 ml.

On y ajoute une solution d'hydroxyde de sodium jusqu'à ce que le pH de la solution soit supérieur à 12. On y verse quelques gouttes de l'indicateur Murexide (purpurate d'ammonium), jusqu'à l'apparition d'une forte coloration rouge. On titre avec une solution $0.1M$ de complexon III, jusqu'à ce que l'indicateur vire au bleu-violet. Soient N ml, la quantité nécessaire pour obtenir le virage. La teneur en molybdène sera:

$$N \times 9.6007 \text{ mg Mo}$$
$$N \times 14.4011 \text{ mg } MoO_3$$

On dissout 37.21 g de complexon III dans un peu d'eau bidistillée et l'on étend à 1000 ml. 1 ml de cette solution correspond à 9.6007 mg de molybdène ou à 14.4011 mg de MoO_3.

On utilise une solution aqueuse saturée de murexide. Il convient de ne pas

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utiliser des solutions plus anciennes que deux semaines. On prépare 100 ml de solution, en dissolvant 0.5 g de la substance solide dans 100 ml d'eau bouillante. Après refroidissement, la solution est prête.

CONCLUSIONS

La détermination du molybdène dans les minerais, par la méthode que nous venons de décrire peut durer 3 à 4 heures. Nous avons pu constater que l'erreur commise (en valeur relative) varie de 0.5% à 0.1% pour les teneurs de 10% à 70% de molybdène. La méthode que nous décrivons sert pour les essais en série d'aciers au molybdène ainsi que pour les minerais. Son intérêt réside surtout dans la rapidité et la facilité de la technique.

RÉSUMÉ

La détermination du molybdène par les méthodes classiques est longue et exige des précautions spéciales. Une méthode simple et rapide est donnée pour les déterminations indirectes du molybdène. La séparation du molybdène (sous forme de molybdate de calcium) est obtenue par précipitation au moyen de chlorure de calcium. Le précipité est dissous dans HCl 1 : 1 chaud. En évaporant la solution, on obtient l'acide molybdique et le chlorure de calcium.

C'est précisément en dosant le calcium par voie complexométrique que l'on détermine indirectement le molybdène. La méthode sert pour les alliages et minerais de molybdène.

SUMMARY

The classical method for the determination of molybdenum is long and requires special precautions. A simple and speedy method is given for indirect determinations of molybdenum. The separation of molybdenum (in the form of calcium molybdate) is obtained by precipitation with calcium chloride. The precipitate is dissolved on adding hot 1 : 1 HCl. On evaporating the solution one obtains molybdenic acid and calcium chloride. In determining the calcium complexometrically one also determines indirectly the molybdenum. This method can be used for the ores and alloys of molybdenum.

ZUSAMMENFASSUNG

Die Bestimmung von Molybdän mit den klassischen Methoden ist lang und erfordert spezielle Vorsichtsmassnahmen. Eine einfache und schnelle Methode ist für die indirekten Bestimmungen von Molybdän gegeben. Die Trennung von Molybdän (als Kalziummolybdat) wird erhalten durch die Ausfällung mit Kalziumchlorid. Der Niederschlag wird durch eine Zugabe von heisser HCl 1 : 1 gelöst. Indem man die Lösung verdampft, erhält man Molybdänsäure und Kalziumchlorid. Indem man nun das Kalzium komplexometrisch dosiert, bestimmt man indirekt das Molybdän. Die Methode geht für die Legierungen und für die Mineralien des Molybdäns.

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MICRO-GRAVIMETRIC DETERMINATION OF LEAD WITH MERCAPTOBENZOTHIAZOLE

by

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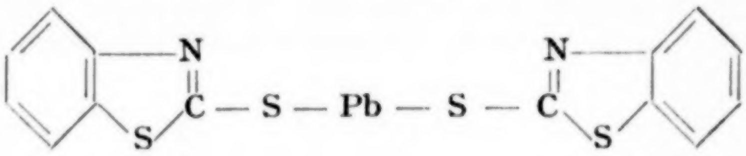
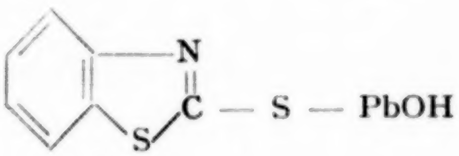
INTRODUCTION

Mercaptobenzothiazole[1] reacts with lead cation, forming two kinds of salts:

a. A normal, yellow salt of the following composition:



2. A white, basic salt having the following structure:



The normal salt is obtained by precipitating lead, in the cold, with an ammoniacal solution of mercaptobenzothiazole. The precipitate, however, is always contaminated with the basic salt. On boiling the normal salt with conc. ammonium hydroxide, it is quantitatively converted into the basic form[2]. The basic salt is also obtained on precipitating lead from a hot neutral solution with an ammoniacal solution of mercaptobenzothiazole.

For the purpose of the quantitative application it is important to obtain the salt in its basic form.

SPACU AND KURAŠ showed in 1936 that lead could be precipitated quantitatively with mercaptobenzothiazole, and evolved a macro-gravimetric method for the determination of lead with this reagent[3].

After studying the various factors affecting this determination, such as: (1) the amount of lead, (2) the volume of the sample, (3) the concentration and amount of the reagent and also the method of its introduction, (4) the digestion of the filtered precipitate with conc. ammonium hydroxide and the volume of ammonium hydroxide used, (5) the filtration, (6) the wash liquid and method used for washing the precipitate, (7) the temperature and time required to dry the precipitate, the authors have elaborated an exact micro-gravimetric method, applying EMICH's[4] micro-technique and using a porcelain filterstick.

EXPERIMENTAL

Reagents and standard solution employed were:

1. Mercaptobenzothiazole solution, 1%, in ammonium hydroxide, 2½%. The solution was prepared by dissolving 1 g of the reagent in 100 ml of ammonium hydroxide, 2½%, heating on the water bath to facilitate solution. It is essential to use a fresh solution, *i.e.* one prepared just before the determination is carried out.
2. Standard $Pb(NO_3)_2$ p.a. solution (the titre of this solution was determined gravimetrically, using the $PbSO_4$ method; it was 3 mg Pb^{+2} per ml).
3. Ammonium hydroxide, 2½%.
4. Ammonium hydroxide, conc.

Remark: The ammonium hydroxide used must be pure and must not give any silica residue on evaporation[5].

5. Cadmium salt solution, 10%.
6. Bi-distilled water.

Procedure recommended for the micro-gravimetric determination of lead

The neutral solution (1-3 ml), containing from 3 to 8 mg lead cation, is introduced into a Pyrex glass micro-beaker (dimensions of the beaker: height 55 mm, outer diameter 18 mm) from a micro-burette graduated to 0.01 ml*. The volume is made up to 3 ml with bi-distilled water, the solution is heated to boiling on an electric hot plate and the beaker immediately transferred to a nearly boiling water bath (a 250 ml beaker full of water and heated on a hot plate).

A 76%-180% excess of an ammoniacal solution of mercaptobenzothiazole, 1%, (Reagent No. 1) is added dropwise from a micro-burette graduated to 0.01 ml (*i.e.* 0.142—0.226 ml are added for each mg of lead present). After the addition of each drop of the reagent, the precipitate formed is stirred with a short, bent glass rod. This rod is attached, by means of a short piece of rubber tubing, to another glass rod serving as a handle during the stirring (Fig. 1 c,d,e).

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* The micro-burette employed was a Blue Line "Exax" burette (U.S.A.) 5 ml capacity, with a graduation interval of 0.01 ml and a platinum alloy delivery tip, giving approx. 100 drops per ml.

The additional glass rod (e) may be removed during the filtering and drying operations, leaving only the bent stirring rod (c) in the micro-beaker. After precipitation, the sides of the beaker and the stirring rod are washed with 2 ml of bi-distilled water, using a wash bottle with a capillary delivery tip. The beaker containing the precipitate is allowed to stand for 10-15 minutes outside the water bath, the additional stirring rod having been removed (Fig. 1 e). The precipitate settles on the bottom of the beaker, while the liquid above it is clarified, becoming transparent and colourless. After the a.m. interval of 10-15 minutes, the precipitate is filtered, using a porcelain filterstick* (Fig. 2) and very low suction. It is most important to keep to the following manner of filtration: the filterplate of the filterstick must merely touch the surface of the clear liquid; as the level of the liquid falls during filtration, the beaker is gradually raised to keep the surface of the liquid just in touch with the filterplate. This prevents the precipitate from being sucked close to the filterplate and, as a result, most of the precipitate is left on the bottom of the beaker, and only a small fraction of it adheres to the filterstick. This manner of filtration is of the utmost importance in order to ensure the complete conversion of the precipitate into the basic salt during its subsequent digestion with boiling ammonium hydroxide, conc. After all the liquid has been filtered off, the filterstick together with the stirring rod and beaker are detached from the suction system, 0.4 ml of conc. ammonium hydroxide (Reagent No. 4) are introduced from a micro-pipette, washing down the sides of the beaker at the

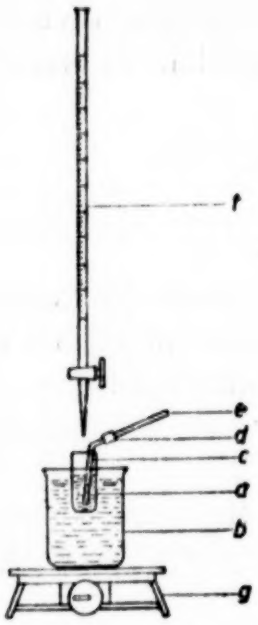

Fig. 1. Apparatus used for precipitation
a. micro-beaker
b. water bath
c. bent glass stirring rod
d. rubber tubing
e. additional glass rod, serving as a handle during the stirring
f. micro-burette
g. electric hot plate

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* The dimensions of the filterstick used were: overall diameter 11 mm; stem diameter 3—4 mm; overall height 55 mm. All filtersticks used were U.S.A. Produce, made by Coors Porcelain Co., Golden.

same time; the beaker is now put into a boiling water bath for 2-3 minutes, while its contents are stirred with the glass stirring rod held with a special forceps (Fig. 3). The colour of the precipitate changes to white. The beaker is next removed from the water bath, allowed to stand for 5 minutes, the precipitate filtered with low suction and washed with a warm ammonium hydroxide solution, 2½% (Reagent No. 3). The wash liquid is introduced from a micro wash bottle with a capillary delivery tip; sides of beaker, filterstick and stirring rod are washed with small amounts of this liquid. Altogether, 4-8 ml of ammonium hydroxide solution, 2½%, are necessary for adequate washing. The filtrate is tested with a cadmium salt solution (Reagent No. 5) for the absence of the precipitating reagent (mercaptobenzothiazole). The filtrate must give no precipitate whatever with the cadmium salt solution. After washing, the micro-beaker containing the precipitate together with the filterstick and the stirring rod, are dried in a drying block of BENEDETTI-PICHLER[6], at 110° C[7] (temperature inside the drying tube; to that end the temperature of the drying block must be 120° C), using low suction. The time required for drying is 25 minutes; after that period, the drying tube containing the beaker, the filterstick and the stirring rod is taken out of the drying block and cooled outside the block for 15 minutes, without interrupting the suction. After cooling, the beaker together with the filterstick and stirring rod are removed from the tube, the beaker wiped, as usual, first with a damp flannel cloth and next with two sets of chamois skins, left for 15 minutes on a nickel block near the microbalance, 5 minutes on a nickel block inside the balance, and finally 5 minutes on the pan of the balance. The beaker, together with the filterstick and the stirring rod, is weighed in the twenty-fifth minute.

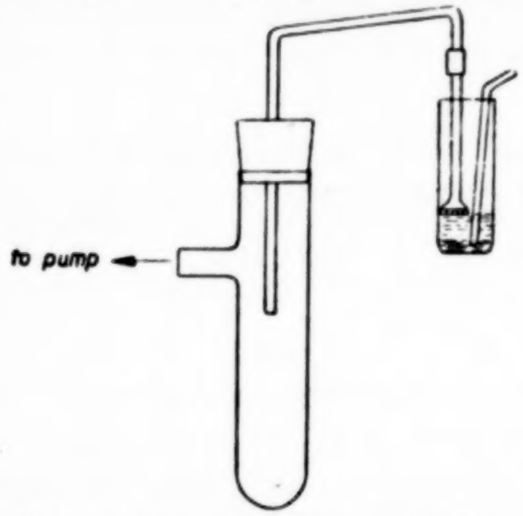

Fig. 2. Apparatus for filtration

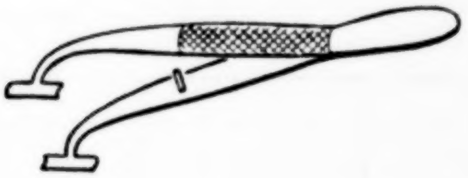

Fig. 3. Forceps

The weight of the precipitate, multiplied by the factor 0.53068*, gives the amount of lead in the sample.

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* The factor given in WELCHER, *loc. cit.*, p. 113, or in PRODINGER, *loc. cit.*, p. 114, is 0.5309. The factor given by the authors, 0.53068, is calculated from the International Atomic Weights of 1952[8].

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The time required for 1 determination is 3 hours approx. (including preparation of the beaker and filterstick); 2 parallel determinations may be carried out in 5 hours approx*.

Cleaning the beaker, filterstick and stirring rod after the determination

The beaker, containing the filterstick and stirring rod, is filled with a warm mixture of HNO_3-H_2O (1 : 1), allowed to stand for 5-10 minutes while the mixture

TABLE I

MICRO-GRAVIMETRIC DETERMINATION OF LEAD WITH MERCAPTOBENZOTHIAZOLE

Exp. No.	Excess of mercapto-benzothiazole solution 1% %	Pb present mg	Pb found mg	Pb difference mg	Relative error %
1	76	3.000	3.009	+0.009	+0.3
2	76	5.010	5.000	−0.010	−0.2
3	76	6.990	6.973	−0.017	−0.2
4	76	8.010	7.989	−0.021	−0.3
5	107	3.000	2.995	−0.005	−0.2
6	107	3.000	3.006	+0.006	+0.2
7	107	5.010	5.011	+0.001	+0.02
8	107	7.020	7.017	−0.003	−0.04
9	107	8.010	7.994	−0.016	−0.2
10	150	3.000	3.009	+0.009	+0.3
11	150	3.000	2.994	−0.006	−0.2
12	150	5.010	5.019	+0.009	+0.2
13	150	5.010	4.996	−0.014	−0.3
14	150	6.990	6.977	−0.013	−0.2
15	150	8.010	8.024	+0.014	+0.2
16	150	8.010	7.987	−0.023	−0.3
17	180	3.000	2.992	−0.008	−0.3
18	180	3.000	3.004	+0.004	+0.1
19	180	5.010	5.018	+0.008	+0.2
20	180	5.010	5.000	−0.010	−0.2
21	180	6.990	6.972	−0.018	−0.3
22	180	6.990	7.005	+0.015	+0.2
23	180	8.010	8.028	+0.018	+0.2
24	107	2.010	2.005	−0.005	−0.2
25	107	2.010	2.015	+0.005	+0.2
26	150	2.010	2.007	−0.003	−0.1
27	150	2.010	2.014	+0.004	+0.2
28	180	2.010	2.015	+0.005	+0.2
29	180	2.010	2.008	−0.002	−0.1

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* 2 mg of lead may also be determined with this method; the excess of the precipitating reagent must, however, be from 107% to 180% (see Table I, exp. No. 24-29). The upper limit is 8 mg, as the determination carried out on 9 mg gives less accurate results under the same conditions.

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is stirred carefully with the filterstick, avoiding any possible injury to the filterplate. The acid is next discarded and the beaker filled with distilled water. The sides of the beaker, the stirring rod and the stem (but not the plate) of the filterstick are cleaned with a rubber policeman. The beaker is now washed, first with 2 × 5 ml of warm HNO_3-H_2O (mixture 1 : 1) and next with 4 × 10 ml H_2O, each time sucking the wash liquid through the filterstick. Drying and weighing of the utensils is done as described under the procedure recommended for the micro-gravimetric determination of lead.

Table I shows some characteristic results obtained by the above method.

Conclusion

As indicated by Table I, results are exact (maximum relative error: $\pm 0.3\%$).

GENERAL DISCUSSION OF FACTORS AFFECTING THE DETERMINATION OF LEAD BY THE PROPOSED METHOD

1. In order to ensure exact results, it is essential to obtain the lead precipitate quantitatively in the basic form. Precipitating from the hot solution, and later boiling the precipitate with conc. ammonium hydroxide, as described in the recommended procedure, makes this entirely feasible.

2. During filtration, the filterplate may barely touch the surface of the liquid, as explained in detail under the procedure recommended.

3. Boiling the precipitate, after filtration, with conc. ammonium hydroxide, must be done in a boiling water bath. Boiling over an open flame or on an electric hot plate, causes the ammonia to volatilise too quickly, before it has a chance of reacting with the precipitate.

4. The efficient stirring of the solution, after each drop of reagent, during precipitation, is essential to the proper agglomeration of the precipitate; where this is neglected, the precipitate tends to stick to the sides of the beaker and its subsequent conversion to the basic form is incomplete.

5. The ammonium hydroxide must be absolutely pure and must, on no account, leave a silica residue after evaporation. Reliance on the analysis of the reagent, as given on the label, is inadequate; the purity of the ammonium hydroxide must be tested experimentally, as its silica content depends on the quality of the glass in which it has been kept and the duration of its storage[5].

6. The mercaptobenzothiazole solution must be freshly prepared just before the determination is carried out, as it remains clear for a few hours only.

PRELIMINARY TEST

The excess of mercaptobenzothiazole solution, 1%, recommended under the procedure elaborated, was 76%—180%. In order to determine the quantity of reagent to be added to a particular sample, the following rapid preliminary test may be carried out:

The neutral lead cation solution (2—3 ml, containing 5—10 mg of lead cation) is introduced into a Pyrex glass test tube (dimensions: length 110 mm, outer diameter 16 mm), from a micro-burette graduated to 0.01 ml. The volume is made up to 8 ml with bi-distilled water, the test tube heated in a boiling water bath and an ammoniacal solution of mercaptobenzothiazole, 1%, (Reagent No. 1) added dropwise from a similar micro-burette. The test tube is shaken and centrifuged for 5 minutes. The precipitate settles to the bottom of the tube and the liquid above it is clarified. The test tube and its contents are heated again, and the reagent again added dropwise to determine whether precipitation has been complete. The shaking, centrifugation, *etc.* are repeated until no precipitate is formed on the addition of the reagent. After 2—3 such experiments, the theoretic amount of reagent, required for this particular sample, may be determined easily, with an average relative error of minus 16%. One preliminary test takes approx. 20 minutes.

Table II shows some characteristic results obtained by this preliminary test.

TABLE II

PRELIMINARY TEST FOR THE CALCULATION OF THE VOLUME OF THE MERCAPTOBENZOTHIAZOLE SOLUTION NECESSARY FOR THE MICRO-DETERMINATION OF LEAD

Exp. No.	Standard Pb solution used	Pb present	Mercaptobenzothiazole solution 1%				Relative error calculated with regard to "theoretic"
			theoretic	used	difference	difference per "ml used"	
	ml	mg	ml	ml	ml	ml	%
1	1.66	4.98	0.402	0.340	—0.062	—0.182	—15.4
2	1.66	4.98	0.402	0.335	—0.067	—0.200	—16.7
3	1.66	4.98	0.402	0.330	—0.072	—0.218	—17.9
4	1.66	4.98	0.402	0.325	—0.077	—0.237	—19.1
5	3.33	9.99	0.806	0.695	—0.111	—0.160	—13.8
6	3.33	9.99	0.806	0.690	—0.116	—0.168	—14.4
7	3.33	9.99	0.806	0.685	—0.121	—0.177	—15.0
					Average:	—0.192	—16.0

Conclusion

As indicated by Table II, the average difference, between the theoretic volume of the mercaptobenzothiazole solution, 1%, and the volume used, is 0.192 ml for each ml participating in the reaction in this preliminary test. This difference amounts to an average relative error of minus 16%, calculated with regard to the theoretic volume of the mercaptobenzothiazole solution.

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DISCUSSION

1. The average relative error of minus 16%, nevertheless, definitely permits the calculation of the quantity of mercaptobenzothiazole which must be added in the final micro-determination of lead. The theoretic volume of mercaptobenzothiazole necessary for the final determination (x ml) may be approximately calculated with the aid of the equation:

$$n + 0.192n = x$$

where n = ml of mercaptobenzothiazole solution, 1%, used in the preliminary test. (The relative error, calculated according to the a.m. equation, for exp. No. 1—7 in Table II, ranges from $\pm 0.7\%$ to $\pm 3.6\%$.)

The effective volume of mercaptobenzothiazole solution, 1%, which must be employed in the final determination of lead (y ml), may be calculated from the following equation:

$$x + ax = y$$

where: a = a coefficient, ranging fron 1.3 to 1.5,

x = the approx. theoretic volume (ml) of mercaptobenzothiazole solution, 1%, required,

y = the effective volume (ml) of mercaptobenzothiazole solution, 1%, required for the determination of lead in a lead solution, equal in volume and lead content to that used in the preliminary test, under the condition that the volume of lead solution used in the preliminary test contained 5—10 mg of lead cation.

The coefficient a (1.3—1.5) relates to 130%—150% excess of mercaptobenzothiazole, which values lie within the 76%—180% optimum range given in the recommended procedure.

2. On the other hand, the preliminary test allows the approx. estimation of the amount of lead cation present in each ml of the lead solution examined (within the same range of relative error, *i.e.*, 0.7%—3.6%), using the equation given below:

$$\frac{10(n + 0.192n)}{0.807\ v} = p \text{ mg lead per ml.}$$

(The condition mentioned under section 1 of this discussion, *i.e.*, that the lead solution employed in the preliminary test contain 5—10 mg of lead cation, also holds here.)

In the above equation:

n = ml of mercaptobenzothiazole solution, 1%, entering the reaction in the preliminary test,

10 = mg mercaptobenzothiazole in 1 ml of a 1% solution,

0.807 = mg of mercaptobenzothiazole reacting with 1 mg of lead; this number is obtained from the ratio:

$$\frac{C_7H_5NS_2}{Pb} = \frac{167.25}{207.21} = 0.807_1$$

v = ml of lead solution employed in the preliminary test.

p = mg of lead per ml of the lead solution examined.

Remark: The above preliminary test, may, therefore, be used as a semi-quantitative method for the determination of lead.

3. Based on the calculation given in section 2, the volume of lead solution to be taken for the final determination of lead may be easily deduced, so that it contains 3—8 mg of lead cation (this being the limits of the micro-gravimetric method recommended).

SUMMARY

The authors have elaborated an exact micro-gravimetric method for the determination of lead with mercaptobenzothiazole.

RÉSUMÉ

Les auteurs ont élaboré une micro-méthode gravimétrique exacte pour la détermination du plomb au moyen de mercaptobenzothiazole.

ZUSAMMENFASSUNG

Die Verfasser haben eine exakte Mikro-gravimetrische Methode zur Bestimmung des Bleis mit Mercaptobenzothiazol ausgearbeitet.

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COMPARATIVE INVESTIGATION OF SOME METHODS FOR THE DETERMINATION OF THE NITROGEN CONTENT OF NITROCELLULOSE

by

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INTRODUCTION

It has been known for a long time that various methods for the determination of the nitrogen content of nitrocellulose do not yield the same results. Therefore the following methods, commonly used in some European countries, were compared, each on two samples.

1. The nitrate determination according to SCHLÖSING.[1]
2. The nitrate determination with the gas volumeter of LUNGE.[2]
3. The nitrate determination by titration with $FeSO_4$ according to LECLERQ AND MATHÉ.[3]
4. Two nitrate determinations according to DEWARDA, differing in method of destruction.

EXPERIMENTAL

Before each determination the nitrocellulose was dried in a current of air at 50-60° C and then for 3 hours in a drying oven at 100° C. The determination according to SCHLÖSING, in which the nitrate is reduced to NO with a strongly acid $FeCl_2$-solution, the NO content being measured, was standardized against pure potassium nitrate. A correction factor is thus found, which is also used for the nitrocellulose.

For the determination according to LUNGE the nitrocellulose is dissolved in sulphuric acid (94.5%); by shaking with mercury the nitrate is then reduced to NO, which is determined volumetrically. Also in this case a correction factor is applied, obtained by standardization against pure KNO_3.

The titration according to LECLERQ AND MATHÉ is based on the same reduction as the method of SCHLÖSING.

According to the first method of DEWARDA the nitrocellulose is dissolved in dilute alkali containing H_2O_2 ("DEWARDA I"); in the second method the nitro-

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cellulose is previously dissolved in acetone and then precipitated with dilute alkali, in which it dissolves again upon being heated ("DEWARDA II"). The results are represented in Table I.

TABLE I

NITROGEN CONTENTS IN % N

	SCHLÖSING	LUNGE	LECLERCQ	DEWARDA I	DEWARDA II
Sample A	12.06	11.98	11.93	12.00	12.05
	12.05	11.92	11.93	12.00	12.05
	12.09	11.95	11.97	11.97	12.04
	12.07	11.92	11.94	11.97	12.04
	12.05	11.94	11.95	11.97	12.03
	12.07	11.95	11.94	11.99	12.03
	12.11				12.03
	12.08				12.00
	12.10				12.01
					12.01
					12.02
					12.00
Mean value:	12.08	11.94	11.94	11.98	12.03
Sample B	13.50	13.29	13.34	13.30	13.44
	13.46	13.27	13.31	13.36	13.43
	13.50	13.28	13.28	13.36	13.44
	13.49	13.28		13.32	13.44
	13.45	13.28		13.35	13.42
	13.49	13.30		13.34	13.41
	13.49			13.37	13.43
	13.48			13.38	13.40
	13.49			13.36	13.41
					13.43
Mean value:	13.48	13.28	13.31	13.35	13.43

One European worker found for the samples A and B according to LUNGE 11.87% and 13.20% N, according to SCHLÖSING 11.85% and 13.18%, respectively. Another European laboratory found for the same samples 12.04% and 13.39% respectively.

COMPARISON OF THE RESULTS

It appears that LUNGE's method yields about the same results as the $FeSO_4$-titration according to LECLERQ AND MATHÉ; this is therefore a confirmation of what the last-mentioned authors suggested. Standardization of the $FeSO_4$-

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solution against pure KNO_3, however, was far less reproducible than titration with nitrocellulose. The satisfactory reproducibility of LUNGE's method and of the $FeSO_4$ titration with nitrocellulose suggests that in both cases the reduction to NO proceeds quantitatively, because otherwise the spread in the results would be far greater. The fact that both methods yield a similar, but lower value than SCHLÖSING's method is therefore probably due to the same cause, *i.e.*, dissolution in concentrated sulphuric acid. For, if the error were due to the reduction mechanism, the methods of LECLERQ-MATHÉ and SCHLÖSING would have to yield the same results, since they are based on the same reaction. The results might be different from the values obtained according to LUNGE. LECLERQ AND MATHÉ point already to the adverse effect of dissolution of nitrocellulose in concentrated sulphuric acid at an excessively high temperature. At 20° C the nitrogen content has dropped very strongly after some hours; at 0° C, however, the decrease would be practically nil. The difference in results between the $FeSO_4$ titration method and that according to SCHLÖSING, however, shows that dissolution of nitrocellulose in concentrated sulphuric acid in unreliable.

Also when comparing the two methods according to DEWARDA the importance of the method of dissolving the nitrocellulose is evident. The reduction is carried out in a completely similar way; dissolution, however, is far more rapid if the nitrocellulose is previously precipitated from acetone.

Destruction invariably entails the risk of nitrogen loss. If, therefore, two methods of analysis use the same reduction mechanism, but render the nitrocellulose ready for analysis in a different way — as for instance the methods of LECLERQ and SCHLÖSING or the two DEWARDA methods — we consider the one giving the highest results the most correct.

The determination according to SCHLÖSING and the method DEWARDA II yield values approaching each other within reasonable limits. However, we prefer SCHLÖSING's method, because it is the only one in which the nitrocellulose is reduced *directly* (*i.e.*, without being previously dissolved).

CONCLUSIONS

1. Dissolving nitrocellulose in concentrated sulphuric acid is by no means a harmless method of destruction. Dissolution in an alkaline medium is highly preferable, though also in this case care should be exercised in view of the results of the two DEWARDA methods.

2. The method of SCHLÖSING is the only one in which the nitrocellulose is reduced without being previously dissolved. Therefore it eliminates a risk of nitrogen loss. Moreover, since the method is more rapid than that of DEWARDA, we prefer it to the latter.

We are indebted to the Management of the Koninklijke Nederlandse Springstoffenfabrieken N.V. for their permission to publish this investigation.

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SUMMARY

A comparison has been made between the methods used in various European countries for the determination of the nitrogen content of nitrocellulose. The results show that the method according to SCHLÖSING is preferable.

RÉSUMÉ

Une étude critique des méthodes (utilisées dans plusieurs pays d'Europe) pour le dosage de l'azote dans la nitrocellulose a été effectuée. On recommande la méthode de SCHLÖSING.

ZUSAMMENFASSUNG

Es wurde eine kritische Untersuchung durchgeführt über die Methoden, welche für die Bestimmung des Stickstoffes in der Nitrozellulose (in mehreren Ländern Europas) angewandt werden. Man empfiehlt das Verfahren nach SCHLÖSING.

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SÉPARATION BARYUM-STRONTIUM PAR CHROMATOGRAPHIE SUR CELLULOSE

I. CHROMATOGRAPHIE SUR BANDES DE PAPIER

par

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INTRODUCTION

Dans le cadre d'un programme de recherche sur les procédés de séparation des produits de fission de l'uranium, nous avons été amenés à rechercher une méthode microchimique de séparation $Ba^{+2}-Sr^{+2}$, applicable aux quantités infinitésimales dites „radiochimiques" en utilisant la chromatographie de partage sur cellulose.

Les méthodes les plus utilisées jusqu'à présent font appel à la coprécipitation[1] ou aux échangeurs d'ions[2]. Dans notre cas, la chromatographie sur bandes de papier nous est apparue comme une méthode de choix pour orienter les recherches. C'est une technique simple, se prêtant bien à la détection chromatographique et aux mesures radioactives; en principe, elle est indépendante des quantités mises en oeuvre.

Différents auteurs[3-8] ont déjà étudié le problème de la séparation chromatographique baryum-strontium sur bandes de papier en se plaçant plus particulièrement au point de vue de la détection des alcalino-terreux entre eux.

Il nous a paru utile d'essayer d'abord d'adapter les techniques des auteurs précités au problème particulier qui nous occupe. Les résultats s'étant avérés peu satisfaisants, nous avons été amenés à faire l'étude d'autres mélanges éluants.

DÉTAILS EXPÉRIMENTAUX-PRODUITS

Nous avons utilisé la technique de la chromatographie descendante en opérant dans des flacons en verre de 30 et 70 cm de haut, la phase saturante est versée dans le fond du flacon. Un joint de porcelaine à débordement interne maintient un secteur en verre portant le godet à éluant; un cristallisoir retourné ferme la partie supérieure et permet un accès facile; une petite lamelle de verre débordant de la cuvette soutient la bande de papier, on doit veiller à ne pas y faire adhérer le papier pour éviter un siphonnage capillaire du liquide éluant.

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Papier. Du papier Whatman No. 1 a été découpé en bandelettes de 30 à 60 cm de long et de 1 à 25 cm de large. La plupart des élutions ont été développées sur une longueur utile de 20 cm; d'autres sur 50 cm et enfin, dans quelques essais, nous avons artificiellement augmenté la longueur en fixant un rouleau du même papier au bas de la bande.

Baryum et strontium. Nous disposions de sels de Ba et Sr activés par irradiation neutronique (Harwell): ^{131}Ba $(NO_3)_2$ (12.1 jours) et ^{89}Sr CO_3 (53 jours). Ces produits „marqués" ont été transformés en chlorures (ou en bromures pour quelques essais). Les quantités utilisées ont varié entre 3 et 180 γ par essai et, afin d'éviter toute confusion possible entre Sr^{+2} et Ba^{+2}, la majorité des essais ont été faits avec des bandes jumelées, chacune portant un seul élément.

Méthodes de détection et de mesure. Après élution, les bandes de papier étaient séchées dans un courant d'air chaud, révélées au rhodizonate, découpées et mesurées avec un compteur de Geiger-Müller type cloche.

Par R_F nous entendrons le rapport de la distance parcourue par la tête de bande comparée à la distance parcourue par le front du solvant.

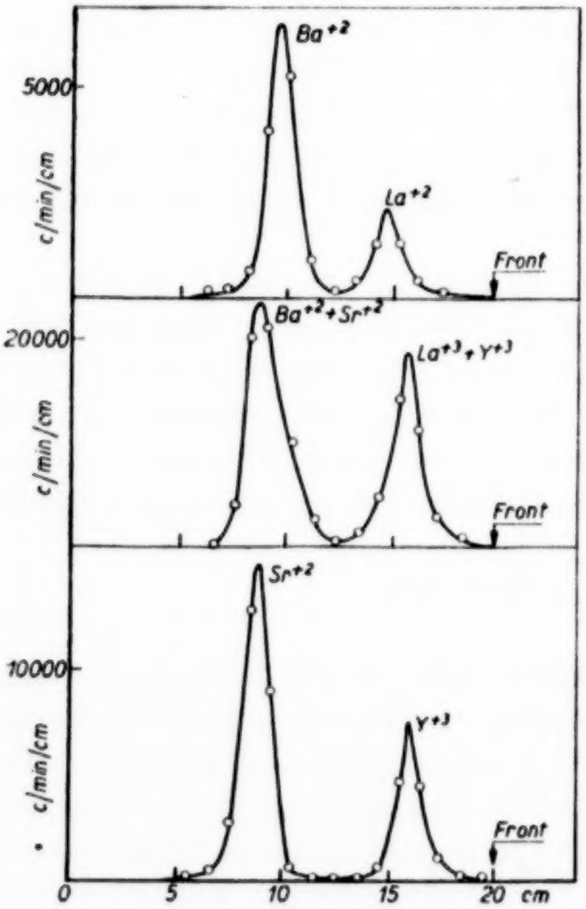

Fig. 1. Eluant: HCl 12 *N*-Butanol (95-5; v/v) saturé en chlorure de butyle.

RECHERCHE DE L'ÉLUANT ADÉQUAT

A. *Essai de la méthode proposée par* C. Miller et R. Magee[3]

Le mélange préconisé est: *n*-butanol — HCl 12*N* (5/95 : v/v) saturé en chlorure de butyle.

Dans ces conditions, avec des quantités de substances supérieures à quelques dizaines de μg, le baryum reste sur place et le strontium migre à mi-chemin du front de l'éluant.

Un examen soigné du phénomène nous a révélé que $BaCl_2$ est tout simplement insolubilisé à l'origine: la solubilité de $BaCl_2$ dans HCl est de 1/20,000[9].

En utilisant des quantités de baryum inférieures à quelques μg, on observe une migration au moins aussi rapide que celle du strontium; à ce sujet la Fig. 1 illustre très bien le phénomène, elle a été obtenue postérieurement à l'aide de

^{140}Ba et ^{90}Sr en „doses traceurs" ($< 1\ \mu$g). Elle prouve qu'il est pratiquement impossible d'obtenir une séparation dans ces conditions; le procédé ne peut donc pas nous convenir et en outre il présente le grave inconvénient de rendre le papier extrêmement fragile.

B. *Essai de la méthode proposée par* F. H. Burstall *et ses collaborateurs*[4]

Ces auteurs recommandent un éluant basique: de la pyridine avec 15-20 % d'eau et 1 % de KCNS; l'atmosphère est maintenue à 70 % d'humidité relative par une solution saturée de NH_4Cl. Ils signalent toutefois des irrégularités de marche qu'ils attribuent à la température. C. Miller et R. Magee[3] signalent ne pas être parvenus à de bons résultats par ce procédé (irrégularité).

Nous avons pensé que les irrégularités de marche pouvaient être dues, au moins en partie, à la présence de CO_2 dans l'air et dans l'eau distillée.

Nos essais tendent à confirmer ce point de vue: l'addition de CO_2 à l'atmosphère de la cuve freine très nettement la marche du baryum et du strontium; le temps de présaturation de la bande modifie également l'allure des séparations et une fraction plus ou moins importante du strontium traîne entre l'origine et le pic proprement dit.

C. *Autres procédés relevés dans la littérature*

Dans un de ses ouvrages traitant de la chromatographie sur papier, Lederer[5] renseigne une série de R_F pour Ba^{+2} et Sr^{+2} avec différents éluants à base de butanol, d'*iso*propanol ou d'éthanol. Dans la plupart des cas, ces R_F sont trop petits (< 0.1).

Pollard et coll.[6] préconisent de la collidine saturée en HNO_3 0.4*N* pour séparer Mg, Ca, Sr, Ba; les R_F respectifs sont 0.65-0.55-0.47-0.40. Ceux de Ba et Sr nous paraissent trop voisins que pour obtenir une séparation nette.

Erlenmeyer et coll.[7] obtiennent 0.43 et 0.55 comme R_F pour Ba et Sr avec de l'éthanol contenant 20 % d'acide acétique 2*N*. Cette différence est encore beaucoup trop petite.

Plus récemment, Surak et coll.[8] ont proposé l'éluant suivant: *iso*propanol-eau-HCl 6*N* (40-30-30: v/v); les R_F sont: Ba: 0.48 et Sr: 0.61.

Nous avons répété cet essai et obtenu des chiffres voisins: 0.57 et 0.65; la différence est aussi trop petite.

D. *Nouveaux essais*

Nous avons procédé à des séries de séparations sur des bandes jumelées, traitées de manière identique, en utilisant l'un des groupes d'éluants suivants:

(1) Elution avec des solutions aqueuses.

(2) Elution avec des solvants variés.

(3) Elution avec des solvants à base de méthanol.

(1) Nous n'avons obtenu aucune séparation avec les éluants aqueux (Tableau I). Les taches sont assez localisées: 2-4 cm pour un développement de 20 cm.

TABLEAU I

Eluant	R_F Ba	R_F Sr	$\varrho = \frac{R_F\,(\text{Sr})}{R_F\,(\text{Ba})}$
HCl *N*/10	0.73	0.73	1.0
Tampon Hexaméthylène-tétramine 0.1*N*	0.93	0.93	1.0
Tampon formique 2/3 *N*.	0.97	0.97	1.0
Tampon acétique *N*/2	0.97	0.97	1.0
Acide formique *N*	0.95	0.95	1.0
NH_4SCN 10 % en poids	0.9	0.9	1.0

(2) *Elution avec des solvants divers.*

TABLEAU II

Eluant			R_F Ba	R_F Sr	$\varrho = \frac{R_F\,(\text{Sr})}{R_F\,(\text{Ba})}$
n-Butanol			0.16	0.27	1.7
Butanol HCl-12*N* (95/5 : v/v)			0.05	0.07	1.4
*Iso*propanol			0.01	0.01	
		(*)	0.01	0.01	
Methanol					
papier séché	à l'air		0.48	0.28	1.7
	à la lampe I.R.		0.5	0.75	1.5
papier prélavé séché à l'étuve	par HCl *N*		0.38	0.46	1.2
Acétone			0.01	0.01	
		(*)	0.01	0.02	
Dioxane			0	0	
		(*)	0	0	
Acétate d'Ethyle			0	0	
		(*)	0	0	

* Le baryum et le strontium étaient déposés sous forme de bromures.

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(3) ***Élution avec des solvants à base de méthanol.*** **Dès le début de nos essais,** nous avions estimé que pour obtenir des séparations, il était préférable de s'adresser à un bon solvant des substances à séparer.

Parmi les produits organiques, le méthanol est un solvant des bromures, chlorures et perchlorates de Ba et de Sr; de plus, sa faible viscosité permet une vitesse d'écoulement plus rapide qu'avec les autres alcools.

Dans les Tableaux III et IV ci-après, nous donnons les valeurs moyennes des R_F trouvés. Le meilleur est celui avec l'acide chlorhydrique; les bandes sont tout juste séparées (révélation au rhodizonate).

Le titre en poids des acides minéraux utilisés est:

HCl — 37 %, HBr — 47 %, HCl — 70 %, HNO_3 — 65 %.

TABLEAU III

Eluant: méthanol = 100 ml	R_F		$\varrho = \frac{R_F\ (Sr)}{R_F\ (Ba)}$
	Ba	Sr	
+ 20 ml acétyl-acétone	0.55	0.77	1.4
+ 1 ml H_2O	0.52	0.88	1.7
+ 5 ml H_2O	0.67	0.9	1.35
+ 10 g NH_4CNS	0.56	0.76	1.35
+ 5 g phénol	0.38	0.65	1.7
+ 5 ml acide formique conc.	0.62	0.77	1.25
+ 5 ml acide acétique glacial	0.53	0.75	1.4

TABLEAU IV

Eluant: méthanol + X (v/v) en ml		R_F		$\varrho = \frac{R_F\ (Sr)}{R_F\ (Ba)}$
		Ba	Sr	
100 + 0.2 ml HBr conc.			0.65	
100 + 0.2 ,, ,, ,,	(*)	0.5	0.65	1.3
100 + 2.5 ,, ,, ,,		0.27	0.5	1.9
100 + 5 ,, ,, ,,		0.21	0.45	2.1
100 + 10 ,, ,, ,,		0.13	0.36	2.8
100 + 20 ,, ,, ,,		0.66	0.185	2.8
100 + 5 ml HCl conc.		0.1	0.3	3.0
95 + 5 ml $HClO_4$ conc.		0.35	0.6	1.7
90 + 10 ,, ,,		0.3	0.65	2.2
75 + 25 ,, ,,		0.17	0.4	2.3
90 + 10 ,, ,,		0.35	0.7	2.0
+ 10 ml H_2O				
100 + 1 ml HNO_3 conc.		0.34	0.72	2.1
100 + 1 ,, ,,	(*)	0.32	0.75	2.3
95 + 5 ,, ,,		0.2	0.5	2.5

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Sur les Figures 2, 3, 4 et 5 nous avons rassemblé des exemples caractéristiques de séparations sur bandes: avec des quantités pondérables de baryum et de strontium on obtient normalement des courbes asymétriques en dent de scie (Fig. 2 et 3) avec des quantités infinitésimales, les courbes deviennent assez symétriques (Fig. 4 et 5).

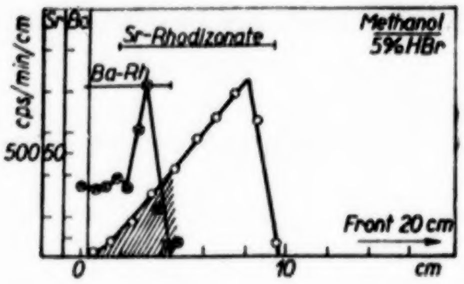

Fig. 2. Eluant: Méthanol-HBr conc. (100/5).

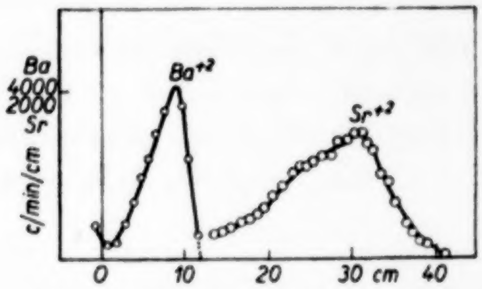

Fig. 3. Eluant: Méthanol-HCl 12 N (100/5) (avec entraineurs).

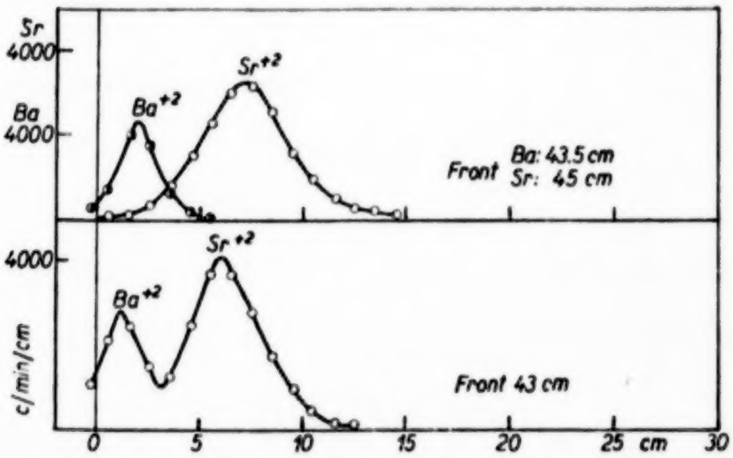

Fig. 4. Bande séparées: Méthanol-HCl 12N (100/5).
Fig. 5. Bande uniques: Méthanol-HCl 12N (100/5) (sans entraîneurs).

Les Figs. 3, 4 et 5 ont été obtenues postérieurement à l'aide des isotopes ^{140}Ba et ^{90}Sr de forte activité spécifique; dans les deux dernières, les substances sont présentes en doses dites radiochimiques.

Il est à remarquer que lorsqu'on désire séparer d'aussi petites quantités de substances, il devient indispensable de laver au préalable le papier avec l'éluant afin d'éliminer certaines impuretés qui fixent les ions ou en retardent la marche d'une manière peu prévisible (surtout pour Ba^{+2}).

Nous avons encore noté qu'avec le mélange éluant méthanol-HCl 12N (100 : 5 v/v) les R_F décroissaient avec la longueur éluée tandis que le rapport $\varrho = R_F$ (Sr) $/R_F$ (Ba) croissait au contraire un peu au delà de 3.0 (bandes de 50 cm et plus).

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CONCLUSIONS

L'examen critique des procédés de séparation Ba-Sr par chromatographie sur papier, proposés dans la littérature, nous a convaincu de la nécessité de rechercher de meilleures conditions:

1. La méthode de MILLER et coll. ne peut guère donner de résultats pour des séparations de quantités inférieures à quelques μg. Pour des quantités supérieures, la séparation obtenue est due simplement à la très faible solubilité du $BaCl_2$ dans HCl concentré.
2. La deuxième méthode, proposée par BURSTALL et coll. n'a pas retenu notre attention tant en raison de l'opinion des auteurs que de nos propres essais. Les vitesses d'élution du Ba^{+2} et du Sr^{+2} sont sujettes à des variations peu contrôlables.
3. Les autres méthodes, proposées dans un but plus général, nous ont paru insuffisantes ou inadéquates et nous ne les avons point retenues.
4. Les essais nouveaux que nous avons entrepris nous permettent d'espérer des résultats concluants pour la séparation de quantités sub-microchimiques de Ba^{+2} et de Sr^{+2} par élution au moyen de mélanges à base de méthanol et d'acide chlorhydrique.

REMERCIEMENTS

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RÉSUMÉ

Pour séparer Ba–Sr en quantités submicrochimiques, nous avons essayé divers procédés de chromatographie sur bandes de papier, proposés dans la littérature, en nous aidant d'isotopes radioactifs. Ces procédés n'ayant pas donné satisfaction, nous avons, par la même technique, recherché une catégorie d'éluants convenables; c'est un mélange méthanol-HCl 12*N* qui nous a donné le plus grand facteur de séparation avec des R_F acceptables et sans trop de recouvrements.

SUMMARY

In order to separate Ba^{+2}–Sr^{+2} in submicroquantities we tested, with the aid of radio isotopes, various paperchromatography methods proposed in the literature. These methods were unsatisfactory for our purpose and therefore we examined some other types of eluants.

A mixture of methanol and 12 N HCl gave the greatest separation factor with a satisfactory R_F value, and without serious overlapping.

ZUSAMMENFASSUNG

Für die Trennung Ba^{+2}–Sr^{+2} in sehr geringen Mengen haben wir, mit Hilfe der radioaktiven Isotopen, verschiedene Prozesse der Papier Chromatographie, die in der Literatur angegeben sind, geprüft. Diese verfahren waren für uns nicht brauchbar, und mit derselben Methode haben wir einige andere Lösungsmittelgruppen untersucht.

Eine Mischung Methanol-HCl 12*N* hat uns den grössten Trennungsfaktor mit brauchbaren R_F und ohne Überlappung gegeben.

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ACTION DU BROMURE DE CYANOGÈNE SUR LE NOYAU PYRIDINIQUE

ÉTUDE SPECTROPHOTOMÉTRIQUE

par

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INTRODUCTION

Les nombreuses difficultés que soulève le dosage spectrophotométrique des principaux dérivés de l'acide nicotinique nous ont incités à entreprendre une étude systématique de la réaction de König. Les résultats acquis[1] offrant la possibilité d'une explication des processus de la réaction, nous avons poursuivi un travail d'identification des dérivés obtenus, en vue d'approfondir le mécanisme de l'action du bromure de cyanogène.

Réaction de König

Cette réaction sur laquelle repose le dosage chimique de l'acide et de l'amide nicotiniques s'effectue, selon les auteurs, en une ou deux étapes:

1 — Action du bromure de cyanogène,

2 — Copulation du produit formé avec une amine aromatique.

En se limitant à la première partie, suivant les conditions du milieu et en particulier le pH, les bandes d'absorption diffèrent en position et en intensité[2,3,4]. Il en résulte une spécificité et une reproductibilité incertaines.

MAXIMA D'ABSORPTION

	Acide nicotinique	Amide nicotinique
HUGHES	3720 A	3520 A
MUELLER	4080 A	3980 A
VACHER	3524 A	3925 A

On peut, *a priori*, soupçonner le rôle déterminant du pH, qui se trouve corroboré par le fait qu'en utilisant la réaction préconisée par VACHER, de la quantité de tampon à pH 5.9 ajoutée dépend la reproductibilité des dosages.

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Telles sont les raisons qui nous ont amenés à étudier les courbes de virage (Tableau I) des principaux dérivés des acides pyridinecarboxyliques en fonction du pH, et à préciser les conditions de reproductibilité des dosages de l'acide et de l'amide nicotiniques[1].

RÉSULTATS EXPÉRIMENTAUX

Nous rapellerons (Tableau I) les résultats obtenus selon le protocole suivant: la solution, tamponnée à pH 5.9, est chauffée 2 min à 80° en présence de bromure de cyanogène; après refroidissement, le pH est modifié entre les valeurs 2 et 13, et parfois plus (réaction de CHAUDHURI[5]).

TABLEAU I

	Forme A (acide)		Forme B (neutre)		pK	Forme C (alcaline)	
	λ_M*	d**	λ_M	d		λ_M	d
Pyridine	3230	0.047	3990	1.8	5	3690	1.2
α-Picoline	3250	0.025	4080	0.08		3735	0.038
γ-Picoline	3500	0.015	4010	0.29		3800	0.05
β-Picoline	—	—	3925	0.56		3965	0.018
2.6-Lutidine	—	—	3950	0.019		3700	0.011
Collidine	—	—	3955	0.030		3700	0.013
Acide *iso*nicotonique	—	—	4050	0.40	7.4	3780	0.26
Acide nicotinique	3515	1.96	3900	2.1	10	3700	1.94
Amide nicotinique	3225	1.1	3925	2.42	4.7	3500 fluorescence	1.38
Coramine	3100	0.375	3960	2.18	4	3630	1.81
Quinoléine	—	—	3900	0.028			

* position du maximum d'absorption en angströms
** les coefficients d'absorption d sont rapportés à 10 µg/ml sous une épaisseur de 1 cm.

On constate:

1. Que les dérivés correspondant à la réaction en milieu acide (dérivés 1) obéissent aux mêmes lois. Les maxima d'absorption sont voisins, situés entre 3000 et 3250 A, sauf en ce qui concerne l'acide nicotinique et la γ-picoline dont le coefficient d'extinction est variable et parfois négligeable (Tableau I).

En solution dans la soude à 5 %, on obtient des dérivés II absorbant vers 3700 A et non fluorescents. Une exception, le dérivé que forme l'amide nicotinique dont le maximum d'absorption se situe à 3500 A et qui est fluorescent.

2. Des différences sont cependant à noter dans les résultats précédents:

La forme acide des dérivés 1 a une intensité faible, sauf en ce qui concerne les

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dérivés substitués en position 3. Le coefficient d'absorption est maximum pour l'acide nicotinique: 1.96.

3. Les courbes de virage obtenues en fonction du pH peuvent être classées en trois groupes: le groupe de celles pour lesquelles la valeur du pK varie entre 4 et 5 (pyridine, nicotinamide, coramine), le groupe de celles pour lesquelles la valeur du pK est voisin de 10 (acide nicotinique) et enfin celui pour lequel le pK est indistinct (dérivés de la pyridine substitués en dehors de la position 3).

Telles sont les conclusions que l'on peut dégager de la présente étude.

ÉTUDE DE LA RÉACTION

En vue d'approfondir le mécanisme de la réaction et de déterminer la structure des dérivés étudiés, nous avons essayé de les isoler.

La principale difficulté rencontrée provient de leur solubilité dans l'eau, plus forte que celle des produits de base.

Nous avons néanmoins pu faire cristalliser un dérivé de l'amide nicotinique et un dérivé de la quinoléine.

Procédé

(a) On ajoute peu à peu une solution de bromure de cyanogène à 10 % dans une solution d'amide nicotinique à 20 % portée à 80° C. Le pH baisse graduellement au cours de la réaction. Lorsque le pH atteint 2.5, on observe une précipitation massive, en même temps que la coloration jaune intense vire à l'orangé. Les aiguilles qui se forment sont essorées et recristallisées par dissolution dans la soude à 2 %, décolorées par addition de noir animal et reprécipitées par une solution d'acide chlorhydrique 4*N*. On essore et on lave les aiguilles jusqu'à l'absence de la réaction des ions Cl^-.

(b) Le dérivé de la quinoléine est obtenu de même, mais, en raison de la faible solubilité de la quinoléine dans l'eau, on emploie une solution saturée à 80° C. Le dérivé obtenu cristallise en magnifiques aiguilles incolores.

Caractéristiques

Dérivé de l'amide nicotinique: F (non corrigé) = 269° C
Dérivé de la quinoléine: F (non corrigé) = 128° C

Analyse élémentaire

Dérivé de l'amide nicotinique:	C	50.2 %
	O	20
	H	4.46
	N	25.17

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Cette composition correspond à la formule brute: $C_7H_7N_3O_2$, celle de l'amide nicotinique étant $C_6H_6N_2O$.

La teneur en azote correspond à celle indiquée par Brusse[6].

Dérivé de la quinoléine:		
	C	69.60 %
	N	16.28
	H	5.38
	O	8.74

Cette composition correspond à la formule brute: $C_{10}H_8N_2O$, celle de la quinoléine étant C_9H_7N.

L'analyse de ces deux dérivés prouve (1) la fixation globale d'HCN et d'O, (2) la non-fixation du brome.

Analyse spectrophotométrique U.V.

Le dérivé de l'amide nicotinique, à notre surprise, ne donne pas le spectre U.V. rencontré dans la réaction habituelle. De plus, on n'observe plus aucune fluorescence lorsque l'on se place dans les conditions que définit Chaudhuri.

TABLEAU II

	Produit de réaction habituel		Produit isolé	
	λ_M	d	λ_M	d
Forme acide	3225 A	1.1	3215 A	1.9
		$pK = 4.7$		$pK = 9.3$
Forme basique	3925	2.42	3765	2.95
Hydrolyse alcaline	3500	1.38	3470	2.5

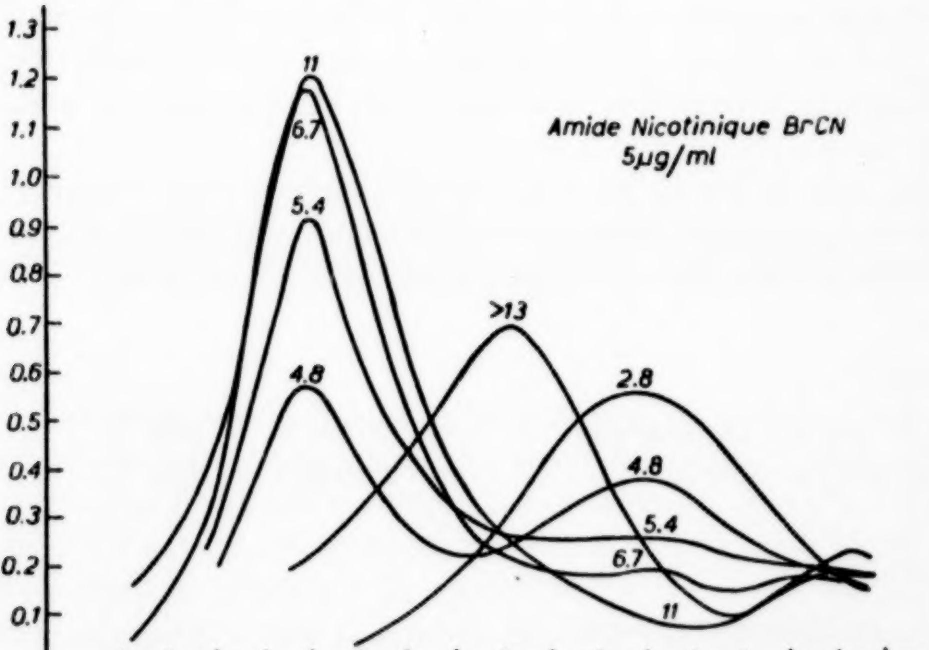

Fig. 1. Amide nicotinique: produit de réaction non isolé.

Les spectres de ces deux dérivés ne diffèrent que par le maximum d'absorption en milieu alcalin et par le pH de demi-neutralisation.

On peut supposer un réarrangement de la molécule.

Dans le cas du dérivé de la quinoléine, on n'observe rien de semblable.

Forme acide: pas d'absorption dans la région 3100-4000 A.

Forme basique: maximum à 3900 A, d = 0.028, pK voisin de 12.

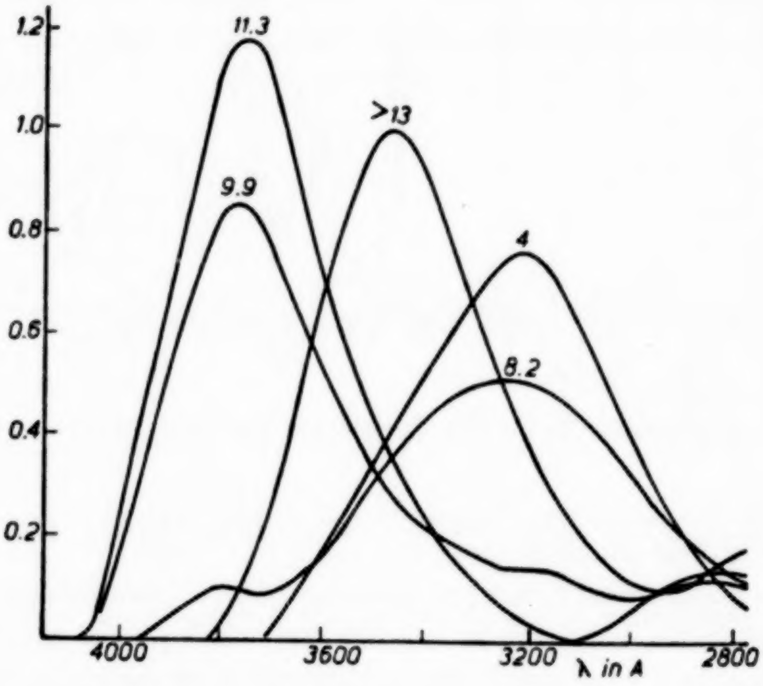

Fig. 2. Amide nicotinique: produit de réaction isolé.

Analyse I.R.

Les analyses ont été effectuées au laboratoire de M. LECOMTE, directeur de Recherches, Sorbonne, sur des poudres ou des mélanges, soit avec de la vaseline, soit avec de l'hexachlorobutadiène.

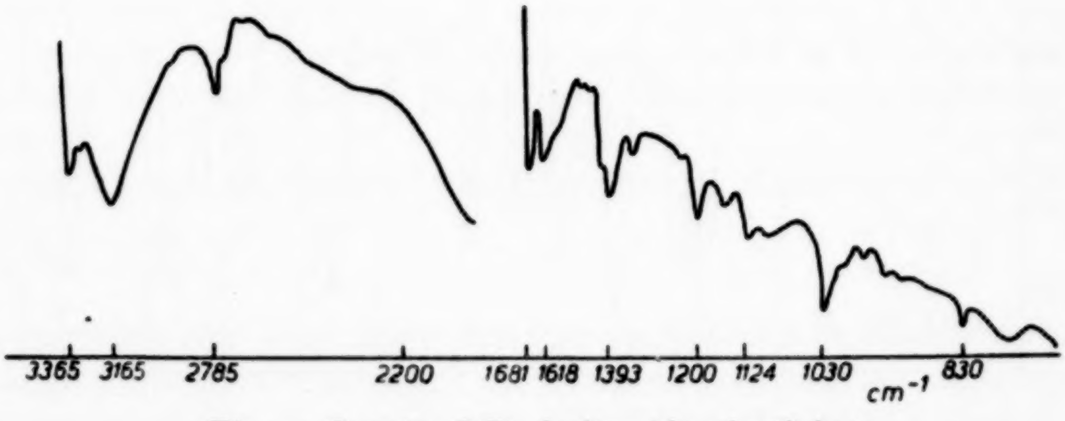

Fig. 3. Spectre I.R. de l'amide nicotinique.

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Dans les deux cas, on relève l'apparition d'une bande d'absorption à 2224 cm^{-1} dans le spectre du dérivé de l'amide nicotinique et à 2233 cm^{-1} dans celui du dérivé de la quinoléine, bande due au groupement $C \equiv N$.

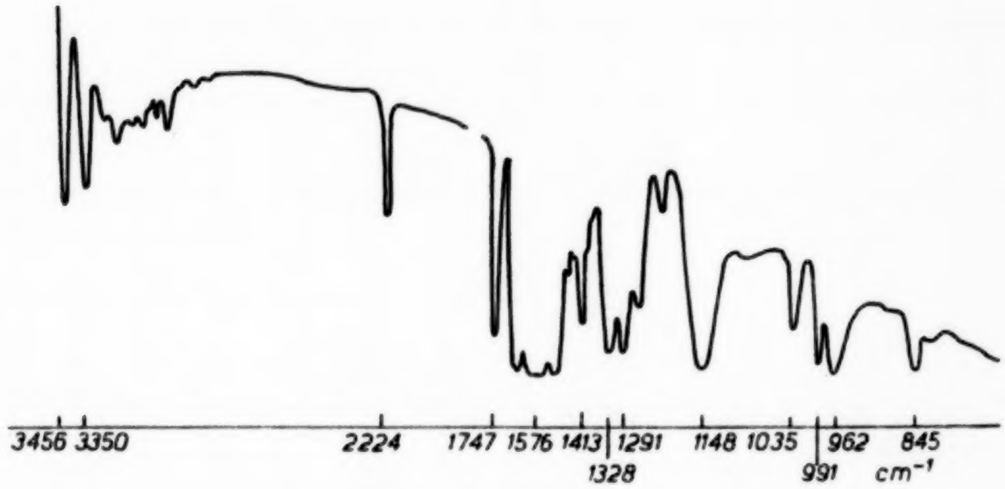

Fig. 4. Spectre I.R. du dérivé de l'amide nicotinique.

— Dérivé de l'amide nicotinique:

Le maintien de nombreuses bandes dues au noyau pyridinique paraît indiquer que ce dernier subsiste. Une bande à 1747 cm^{-1} indique la présence d'un $C=O$ cyclique et une bande à 1148 cm^{-1} une substitution en méta, donc la présence du groupement $C \equiv N$ sur l'azote. La bande à 3455 cm^{-1} semble indiquer la présence d'un OH.

On serait donc en présence d'une 1-cyanonicotinamidipyridone ou d'un corps très voisin. Le point de fusion du corps, 269°, et son spectre U.V. peuvent être

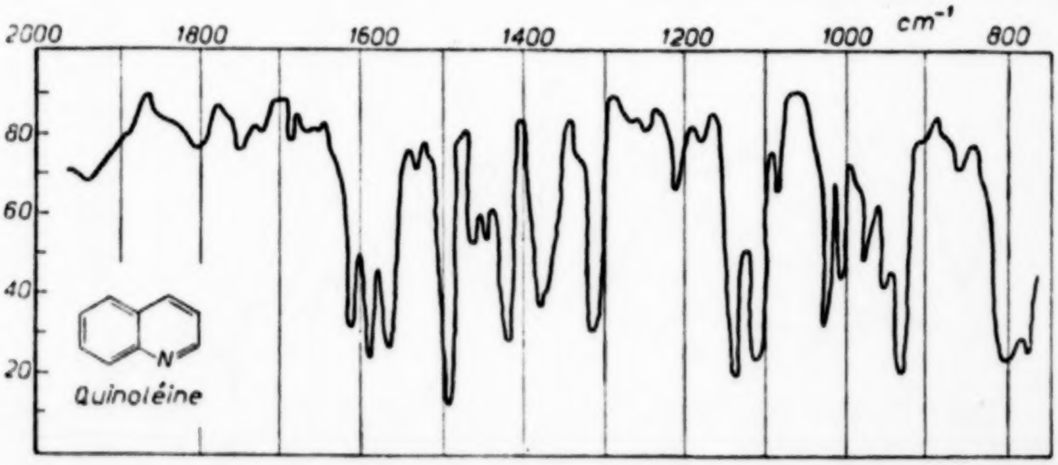

Fig. 5. Spectre I.R. de la quinoléine (R. B. BARNES, *Infrared Spectroscopy*, p. 98). *Bibliographie p. 247.*

rapprochés de ceux observés par PULLMAN[7] pour la 1-méthylnicotinamide-2-pyridone (222°, 3300 A).

— Dérivé de la quinoléine:

On ne relève pas de bande à 3500 cm^{-1}. Celle à 1661 cm^{-1} paraît faire partie des trois bandes que l'on rencontre déjà dans cette région dans le cas de la quinoléine.

Dans la région de 1200 cm^{-1}, on observe une bande à 1177 cm^{-1} due à $=$C-O et une autre à 1050 cm^{-1} due à OH.

Des bandes à 750 cm^{-1} et 780 cm^{-1} révèlent une trisubstitution voisine, donc le C$\equiv$N sur l'azote.

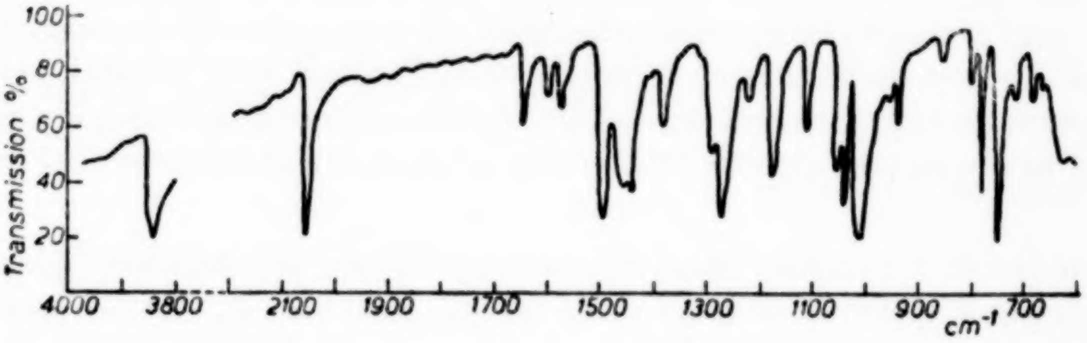

Fig. 6. Spectre I.R. du dérivé de la quinoléine.

CONCLUSIONS

A. L'étude des courbes de virage des principaux dérivés de l'acide nicotinique permet de déterminer les domaines de pH permettant d'effectuer les dosages avec une absolue garantie de reproductibilité.

La spécificité peut être obtenue:

(1) pour l'acide nicotinique, par la mesure de l'absorption à 3515 A en milieu de pH 2-3. En présence d'amide nicotinique, ce pH est le seul qui convienne pour l'application de la méthode de photométrie hétérochrome en bande étroite de VACHER.

(2) pour l'amide nicotinique, par le dosage par fluorescence en milieu très alcalin.

B. Il n'existe pas plus d'unanimité dans l'interprétation de la réaction du bromure de cyanogène que nous n'en avions rencontré sur les conditions de dosage.

C'est que la plupart des auteurs ont déduit leurs formules de l'analyse de la

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réaction au sein même de la solution. Seul, BRUSSE avait isolé le produit que donne l'amide nicotinique, et il semble bien que celui que nous avons obtenu soit identique au sien. Ses résultats étaient fragmentaires; c'est la raison pour laquelle nous avons procédé aux recherches précédentes. Dès l'abord, on peut, au vu des courbes de virage en fonction du pH, par la mise en évidence des formes réversibles, exclure l'hypothèse d'une large ouverture du noyau pyridinique.

Ensuite, sans rejeter catégoriquement l'ouverture partielle du noyau en position 1-2, on peut penser que la réaction essentielle consiste en une oxydation.

L'absence de brome dans la molécule, la fixation confirmée du groupement $C{\equiv}N$, l'existence supposée d'après l'investigation infrarouge d'un groupement $C{=}O$, corroborent cette hypothèse. Bien que le fait que le produit cristallisé donné par l'amide nicotinique ne corresponde pas à celui dont on étudie les propriétés en solution et que ceci ne nous autorise qu'à des suppositions, on peut penser que l'action du bromure de cyanogène s'apparente à celle des ferricyanures alcalins. La transformation en pyridone et la fixation d'un groupement $C{\equiv}N$ expliqueraient seules le domaine de l'absorption, les modifications que provoque la variation du pH pouvant être attribuées à un changement de forme des fonctions.

(Nous tenons à remercier Mme DELIGNE, spécialiste de laboratoire, pour l'aide qu'elle nous a apportée au cours de ce travail, ainsi que M. HADNI, qui a bien voulu se charger des analyses I.R.)

RÉSUMÉ

La présente étude a pour objet les conditions de spécificité et de reproductibilité requises pour le dosage spectrophotométrique des dérivés de l'acide nicotinique. Les courbes de virage de ces dérivés, obtenues en fonction du pH, permettent de préconiser des méthodes répondant aux conditions énumérées ci-dessus.

La deuxième partie du travail a trait au processus par lequel le bromure de cyanogène rend possible l'absorption ou la fluorescence. A cet effet, le produit de réaction de l'amide nicotinique, isolé, a été analysé. L'analyse quantitative, les spectres U.V. et I.R., nous amènent à des hypothèses sur l'attaque du noyau pyridinique.

SUMMARY

The object of this investigation was to study the conditions of specificity and reproducibility required for the spectrophotometric determination of nicotinic acid derivatives. The end-point curves of these derivatives, obtained as a function of pH, make it possible to choose the methods which correspond to the conditions enumerated above.

The second part of the work deals with the process by which cyanogen bromide enables absorption or fluorescence. For this purpose, the isolated reaction product of the nicotinic amide was analysed. The quantitative analysis, the ultraviolet light and infrared spectra lead us to the theory that the pyridine ring is attacked.

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ZUSAMMENFASSUNG

Die vorliegende Arbeit befasst sich mit den Bedingungen für die erforderliche Spezifität und Reproduktibilität der spektrophotometrischen Bestimmung der Derivate der Nikotinsäure. Die Kurven für die Färbung dieser Derivate, welche man in Funktion verschiedener pH-Werte erhält, ermöglichen die Wahl von Methoden, welche den genannten Erfordernissen entsprechen. Der zweite Teil der Arbeit befasst sich mit dem Vorgang, durch welchen das Bromcyan die Absorption oder die Fluoreszenzmessung ermöglicht. Zu diesem Zwecke wurde das isolierte Reaktionsprodukt des Nikotinsäureamid analysiert. Die quantitative Analyse, die Ultraviolet- und Infrarotspektren führen uns zur Annahme, dass der Pyridinring angegriffen wird.

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THE HETEROMETRIC MICRO-ANALYSIS OF COBALT WITH α-NITROSO — β-NAPHTHOL.

A GENERAL STUDY.

by

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The precipitation of cobalt with α-nitroso-β-naphthol (= "$\alpha\beta$") was one of the first methods used for the determination of a metal with the help of a *selective* organic reagent [1]. This substance and dimethylglyoxime are the best and the most sensitive reagents yet available for the gravimetric determination of cobalt or nickel. Both form the gateway to the modern analytical chemistry of organic reagents for metals. Although they are not so versatile in application as oxine, their use is unique for the determination of cobalt and nickel. Previously, we have reported heterometric studies using dimethylglyoxime and nickel. In this and the following report we use the heterometric method to study the compounds which are obtained between cobalt and $\alpha\beta$, their composition, behaviour and analytical application.

ILINSKI AND VON KNORRE investigated the reaction between Co^{+2} and $\alpha\beta$ and studied the behaviour of the compounds obtained. With $\alpha\beta$-Na and excess of Co^{+2} they obtained an insoluble compound which, after drying, has the composition $[C_{10}H_6O(NO)]_2Co$. Cobalt, which was precipitated with $\alpha\beta$-alcoholic or $\alpha\beta$-acetic acid solutions, gave a compound which was very stable towards alkali, acids, oxidation or reduction. According to these authors, the compound obtained is soluble in concentrated HNO_3 or H_2SO_4, but is then precipitated again from the solution by the addition of water. They accepted the view that the cobalt exists in the compound in the *tri*valent state.

MAYER AND FEIGL claim that cobalt in the precipitate is present partly in the divalent and partly in the trivalent state. They obtained a precipitate of Co-$\alpha\beta$, by dissolving $Co(OH)_3$ in concentrated acetic acid which gave, after drying at 130° C, the composition $CoR_3.2H_2O$.

KOLTHOFF AND LANGER made a further amperometric study and expressed their doubts of the formula given by FEIGL. From a NH_4Cl/NH_3 solution they obtained a brown precipitate which gave the ratio 1 Co: 2.8 $\alpha\beta$, but the results were not very reproducible. When titrated (in 0.1*N* KCl), a ratio of 1 Co : 2 $\alpha\beta$ was obtained. On the addition of an excess of H_2O_2 to the ammoniacal cobalt

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solution, the colour turned a dark reddish brown, but no precipitate was formed upon the addition of the reagent. On the other hand, they found that upon the addition of acetic acid to $Co(OH)_3$ at room temperature, the greatest part of the cobaltic cobalt was reduced to the bivalent state. They carried out very many gravimetric determinations of cobalt-$\alpha\beta$-precipitates which were obtained under different working conditions and dried at 135° C. Precipitated from a strong acetic acid solution, the composition varied between $CoR_{3.5}$ and CoR_4; from an ammoniacal solution the composition was CoR_3. These authors state: "... no indication has been obtained, that cobalt in the precipitate obtained in the acid medium is present in the trivalent form". According to them, the effect of nickel upon the amperometric results needs further study.

The solubility of Co-α-nitroso-β-naphthol and Co-β-nitroso-α-naphthol is given by CACCIAPUOTI AND FERLA as 1.5 and 0.17 mg per liter. KOMAR AND TOLMACHEV worked with Co^{+2} and nitrosophenol (in various concentrations). By the use of the Job procedure they obtained always a maximum optical density at the ratio of 1 Co: 2 nitrosophenol (= CoR_2). Working with excesses of Co^{+2} the equilibrium constant was found to be $5 \cdot 10^{-17}$. In excess of nitrosophenol the constant was considerably higher and this was attributed to the formation of CoR_3 which has a solubility product of $2 \cdot 10^{-24}$.

The problem of the composition and behaviour of Co-α-nitroso-β-naphthol compounds, which were obtained by changing the medium or other working conditions, were studied by us *heterometrically*. Many experiments were carried out with cobaltous and cobaltic solution simultaneously in order to make a comparative study. In all cases the analytical side was specially considered. The conclusions drawn are shown later in this report.

From the results obtained it can be seen that the sensitivity of the Co-α-nitroso-β-naphthol heterometric determination is very high; it is several times more sensitive than the determination of nickel with dimethylglyoxime. In addition, the maxima density values which are obtained for a definite amount of cobalt, remain unchanged in the presence of masking agents and foreign metals (even in a concentration of 99%).

EXPERIMENTAL

The method and apparatus used were the same as described in previous reports.[2] The α-nitroso-β-naphthol (= "$\alpha\beta$") was a BDH reagent "for spot test". The other chemicals were either analytical reagents or chemically pure. The $\alpha\beta$ alc. was obtained by dissolving in redistilled alcohol (the solution remains unchanged for several months). All heterometric titrations were thermostatically controlled and were carried out at 20° (± 0.1°) C. Here, as in other heterometric determinations, no controlled temperature is necessary, as the accuracy of the determination is independent of room temperature. In contrast to this, the maxima

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density *values* are influenced by the room temperature. By controlling the latter, the values obtained at different times and under different working conditions may be better compared with each other. The analysed volume was in all cases equal to 20 ml and contained between 0.15 and 0.44 mg cobalt. The analysed cobalt concentration was between 0.000125*M* and 0.0004*M*.

RESULTS

General

The following tables and figures represent a fraction of the titrations made. They show the results obtained with cobalt in the absence of foreign metals. The time required for a titration, the other constituents being identical, depends on the amount of cobalt present and on the acidity of the solution. It appears that the time increases with rising acidity. A titration generally took about 15-20 minutes. In extreme cases it took about three times as long. The average error amounted to 1-2% (0.1-0.5 γ/ml) and in more extreme cases it amounted to 3%.

Influence of the medium, acidity and added substances

Cobalt solutions containing acids, metal complex binders and neutral salts etc. were titrated heterometrically with 0.0033*M*-0.01*M* $\alpha\beta$. In some cases the water medium was replaced by 50% alcohol.

Table I presents a compilation of the results obtained (the numbers are the same in the Tables and in the Figures). Generally it may be said that the sensitivity is higher in the alcoholic solution. In a water solution (exp. 3) the minimum amount of cobalt which could be used was 5 ml 0.00075*M* and the maximum density value obtained was low. Under the same working conditions in alcoholic solution, even with 5 ml 0.0005*M* cobalt, a high density value was obtained

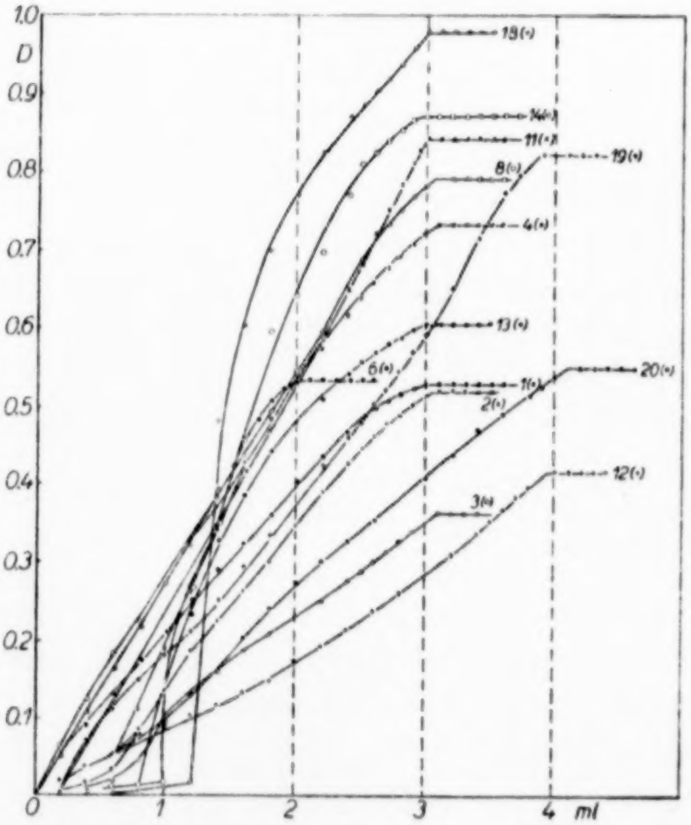

Fig. 1.
Titrations of $Co(NO_3)_2$ with α-nitroso-β-naphthol in alcohol under different working conditions.

(exp. 13). The same may be seen when working in a neutral solution (exps. 12 and 19). Solutions of higher acidity may be used in 50% alcohol than in water solutions, which give similar maxima values (exps. 11 and 18). With regard to the time required for a titration, we see that, in general, less time is required working in slightly acid, neutral or slightly alkaline solutions (exps. 1, 5, 7, 8, 12 and 15). This of course also depends on the concentration of cobalt: the more dilute the analysed cobalt solution, the longer the time of titration. The longest titration times required are when working in aqueous acid solution (exps. 4, 6, 9, 10 and 11). As to the point (on the abscissa) of the *initial* precipitation, the following may be said: the solubility is greater in acid solution than in neutral; the influence of the medium is not detectable; in the more dilute solutions of cobalt in alcoholic solution, the initial precipitation occurs of course later (exp. 13, 14). But even in the most diluted cobalt solution, the point of the *initial* precipitation still lies far away from the first point of maximum density. It is interesting to note that H_2O_2 in neutral water solution has no influence on the results. The same is so in the case of a *water* solution which contains K_2-tartrate and in any citrate solution (exps. 4, 5, 6 and 19). This is in contrast to the behaviour of an *alcoholic* concentrated solution of K_2-tartrate (see below).

Further results of specific titrations are as follows. Na_3-citrate or K_2-tartrate (1 ml M) has no influence when added to the acetic acid water solution (exps. 4, 6). The same is the case in the presence of Na-acetate (exps. 1, 5). HCl, H_2SO_4 and H_3PO_4 (1 ml 0.1M) may be added to the water solution (exps. 9, 10, 11). In 50% alcohol, H_3PO_4 may be added in even higher concentration (1 ml M) (exp. 18) but HCl or H_2SO_4 (1 ml M) prevents the precipitation of Co (exp. 17). The addition of NH_4NO_3 to the acetic acid 50% alcoholic solution increases the maximum density value (exps. 13, 14). The same effect is obtained by the increase of the pH through the addition of Na-acetate. The errors obtained are between zero and 3%. No clear relation exists between the cobalt concentration and the error in %. Under all experimental conditions the maximum density value lies at the molar ratio of 4 $\alpha\beta$: 1 Co.

Influence of potassium tartrate

The results of heterometric titrations of Co^{+2} in 50% alcoholic solutions in the presence of K_2-tartrate are very striking. Table II, exps. 1-4 and Fig. 2 show some of the results obtained. Whilst in the *dilute* tartrate solution (exp. 2) the molar ratio at the first maximum point is equal to 1 Co: 4 $\alpha\beta$, in the more concentrated tartrate solution this ratio is equal to 1 Co : 2 $\alpha\beta$ (exps. 1, 4). In all cases the error is less than 2%. Both results can be used for a quantitative determination of minute quantities of cobalt. With regard to the composition of the compound which is obtained in *concentrated* tartrate, it is difficult to tell whether it contains tartrate or consists solely of CoR_2.

TABLE I

Composition: 5 ml $Co(NO_3)_2$ aM + 15 ml supplements + x ml α-nitroso-β-naphthol alc. bM Temp. = 20° (± 0.1°) Filter: red

Exper. number	Supplements	molarity		Co in mg	$\frac{[\alpha\beta]}{[Co]}$	x ml		Initial precip. at ml	Maxim. density	Approx. titration time in min.	Error		
		$\alpha\beta$*	Co**			content	found				%	γ	γ/ml
1	1 ml Na-acetate M + 14 ml H_2O	0.01	0.0015	0.44	4:1	3.0	3.0	0.0	0.53	7	0.0	0.0	0.0
2	1 „ CH_3COOH „ + 14 „ „	0.0066	0.001	0.29	4:1	3.0	3.02	0.4	0.52	23	+0.7	2.0	0.1
3	1 „ „ „ + 14 „ „	0.005	0.00075	0.22	4.1:1	3.0	3.1	0.4	0.36	35	+3.3	7.3	0.4
4	1 „ „ „ + 1 „ Na-citrate M + 13 ml H_2O	0.0066	0.001	0.29	4:1	3.0	3.05	0.2	0.73	53	+1.6	4.6	0.2
5	1 „ Na-acetate „ + 1 „ Na-citrate „ + 13 „ „	0.01	0.0015	0.44	4.1:1	3.0	3.1	0.0	0.57	8	+3.3	14.5	0.7
6	1 „ CH_3COOH „ + 1 „ K_2-tartrate „ + 13 „ „	0.01	0.001	0.29	4:1	2.0	1.97	0.0	0.53	31	—1.5	4.4	0.2
7	2 „ „ „ + 2 „ $H_2O_2 M$ + 1 ml NH_3 M + 10 ml H_2O	0.01	0.0015	0.44	4:1	3.0	3.02	0.0	0.47	11	+0.7	3.1	0.15
8	2 „ NH_4NO_3 „ + 2 „ H_2O_2 „ + 11 ml H_2O	0.01	0.0015	0.44		3.0	3.02	0.0	0.79	16	+0.7	3.1	0.15
9	1 „ HCl 0.1M + 14 ml H_2O	0.01	0.0015	0.44	4.1:1	3.0	3.06	∼0.6	0.79	38	+2.0	8.8	0.4
10	1 „ H_2SO_4 0.1M + 14 ml H_2O	0.01	0.0015	0.44	4:1	3.0	3.05	0.4	0.82	30	+1.7	7.2	0.4
11	1 „ H_3PO_4 0.1 M + 14 „ „	0.01	0.0015	0.44	4:1	3.0	3.01	0.4	0.84	32	+0.3	1.3	0.06
12	1 „ Na_3citrate M + 14 „ „	0.005	0.001	0.29	4:1	4.0	3.94	0.0	0.41	20	—1.5	4.4	0.2
13	1 „ CH_3COOH M + 10 ml alc + 4 ml H_2O	0.0033	0.0005	0.15	4:1	3.0	2.98	0.8	0.61	25	—0.7	1.1	0.05
14	1 „ „ „ + 2 „ NH_4NO_3 2N + 2 ml H_2O + 10 ml alc.	0.0033	0.0005	0.15	3.8:1	3.0	2.90	0.8	0.87	22	—3.3	5.0	0.25
15	1 „ „ „ + 1 „ Na-acetate M + 3 ml H_2O + 10 ml alc.	0.0033	0.0005	0.15	3.8:1	3.0	2.90	0.4	0.89	15	—3.3	5.0	0.25
16	5 „ H_2O + 10 ml alc.	0.0033	0.0005	0.15	3.9:1	3.0	2.96	0.6	0.73	16	—1.2	1.8	0.09
17	1 „ HCl M (or 1 ml H_2SO_4 M) + 4 ml H_2O + 10 ml alc.	0.01	0.0015	0.44									
18	1 „ H_3PO_4 M + 4 ml H_2O + 10 ml alc.	0.01	0.0015	0.44	4:1	3.0	3.02	1.2	0.98	29	+0.7	3.1	0.15
19	1 „ Na_3citrate M + 9 ml H_2O + 5 ml alc.	0.005	0.001	0.29	3.8:1	4.0	3.84	0.0	0.82	28	—4.0	11.6	0.6

* $\alpha\beta$ = α-nitroso-β-naphthol

** Co = $Co(NO_3)_2$

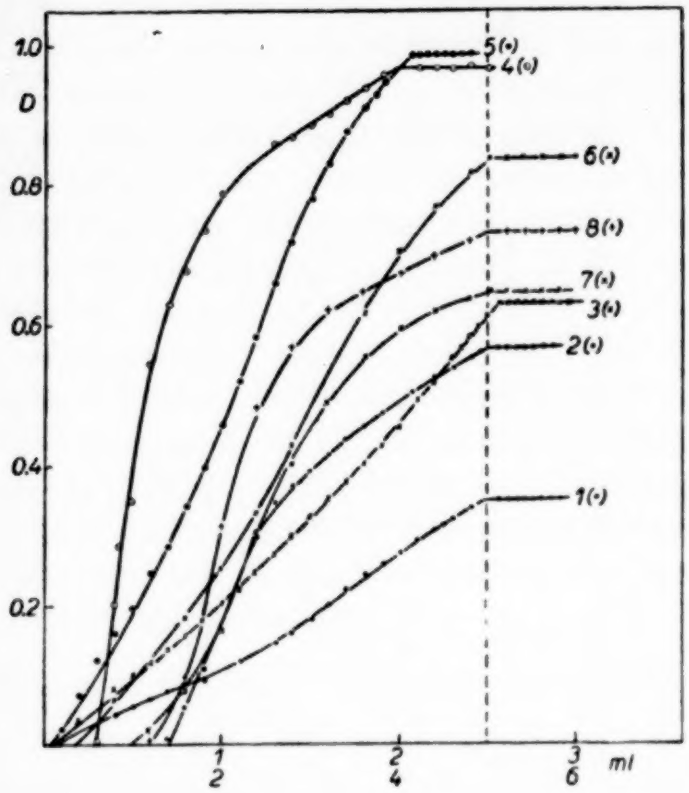

Fig. 2. Titrations of $Co(NO_3)_2$ or α-nitroso-β-naphthol in water or alcoholic milieu.

Influence of di-sodium-ethylenediaminetetraacetate

Experiments were carried out in order to investigate the influence of EDTA-Na_2 on the course of the precipitation of Co-α-nitroso-β-naphthol. EDTA-Na_2 was added in excess to the $Co(NO_3)_2$ solutions and then the cobalt was titrated with an alcoholic solution of α-nitroso-β-naphthol as usual. Parallel experiments were carried out in alkaline, neutral and acidic solutions. In no case was a precipitate formed. Suspensions of Co-α-nitroso-β-naphthol were obtained by titrating a solution of $Co(NO_3)_2$ with α-nitroso-β-naphthol up to the maximum optical density. These suspensions were then titrated with EDTA-Na_2-solution. It turned out that the maximum density *values* remained unchanged by the addition of EDTA-Na_2.

Reverse titrations of αβ with cobalt

Table II and Fig. 2 present a series of such titrations. If we compare the molar concentrations of αβ with those of Co^{+2} used for a titration, we find that they are between 2 and 5 times as great. This is to be expected as in all titrations the molar ratio at the maximum density point is equal to 1 Co : 4 αβ. With the exception of exp. 5, with its high maximum value, the error is less than 2 %. In the 65% alcoholic solutions (exps. 8, 9), theoretical values were obtained although the solubility of the precipitate is higher in these solutions. Alcoholic solutions of α-nitroso-β-naphthol may therefore be standardized with a dilute water solution of cobalt nitrate (0.001*M*-0.002*M*) and the error is low or equal to zero.

Titrations of cobalt with αβ in 50% acetic acid solution

Table III and Fig. 3 contain a small selection of such titrations which were carried out either with a $Co^{II}(NO_3)_2$ solution or with a water solution of $Na_3Co^{III}(NO_2)_6$. The Co^{+2} concentration in exps. 1 and 2 is similar to that which was used for the titration of Co^{+2} with αβ in alcoholic solution. Practically the

TABLE II

Composition: 20 ml solution + x ml α-nitroso-β-naphthol alc. or $Co(NO_3)_2$. Temp. = 20° (± 0.1°). Red filter.

Exper. number	Content	Molarity		mg	$\frac{[\alpha\beta]}{[Co]}$	x ml		Initial precip. at ml	Maxim. density	Approx. titration time in min.	Error		
		$\alpha\beta$ *	Co **			content	found				%	γ	γ/ml
1	5 ml Co + 1 ml CH_3COOH M + 1 ml K_2-tartrate M + 3 ml H_2O + 10 ml alc. + x ml $\alpha\beta$ alc.	0.001	0.0005	Co: 0.15	2:1	10.0	5.02	0.4	0.35	16	50.2		
2	5 ml Co + 1 ml CH_3COOH M + 1 ml K_2-tartrate 0.1M + 3 ml H_2O + 10 ml alc. + x ml $\alpha\beta$ alc.	0.002	0.0005	0.15	4:1	5.0	4.96	1.5	0.57	30	1.0	1.5	0.07
3	5 ml Co + 1 ml CH_3COOH M + 4 ml H_2O + 10 ml alc. + x ml $\alpha\beta$ alc.	0.002	0.0005	0.15	4:1	5.0	5.08	0.4	0.62	32	1.6	2.4	0.1
4	5 ml Co + 1 ml CH_3COOH M + 1 ml K_2-tartrate M + 3 ml H_2O + 10 ml alc. + x ml $\alpha\beta$ alc.	0.0025	0.001	0.29	2:1	8.0	3.94	0.7	0.97	11	49.3		
5	5 ml $\alpha\beta$ alc. + 1 ml CH_3COOH M + 14 ml H_2O + x ml Co	0.005	0.0015	$\alpha\beta$: 4.33	4.1:1	4.17	4.04	0.0	0.99	17	+3.2	139	7
6	3 ml $\alpha\beta$ alc. + 1 ml CH_3COOH M + 16 ml H_2O + x ml Co	0.005	0.0015	2.60	4:1	2.5	2.46	0.0	0.84	21	−1.6	41.6	2.1
7	3 ml $\alpha\beta$ alc. + 1 ml CH_3COOH M + 6 ml H_2O + 10 ml alc. + x ml Co	0.005	0.0015	2.60	4:1	2.5	2.5	0.6	0.65	16	0.0	0.0	0.0
8	3 ml $\alpha\beta$ alc. + 1 ml CH_3COOH M + 5 ml NH_4NO_3 2N + 1 ml H_2O + 10 ml alc. + x ml Co	0.005	0.0015	2.60	4:1	2.5	2.5	0.6	0.73	20	0.0	0.0	0.0

* = α-nitroso-β-naphthol
** Co = $Co(NO_3)_2$

same results are obtained in both kinds of titrations. The maximum values are lower than those which were obtained in 50% alcoholic solutions. In both cases (Table III, exps. 1, 2, and Table I), the molar ratio at the point of maximum is 1 Co: 4 $\alpha\beta$. There is no advantage in working in 50% acetic acid; on the contrary, the sensitivity of the reaction is higher in 50% alcoholic solution. The percentage error is of the same order as in some titrations with $\alpha\beta$ in alcohol.

Table III presents in addition three titrations of a $Na_3Co^{III}(NO_2)_6$ solution with $\alpha\beta$ (in 50% acetic acid) (exps. 3-5).

If we compare exps. 1 and 2 with 3-5, we find that in both cases the maxima values obtained with equal amounts of cobalt are of the same magnitude, although the molar ratios of Co: $\alpha\beta$ at the maxima, are, in exps. 1 and 2 equal to *four* and in exps. 3-5 equal to *three*. *Although different reactions may take place between* Co^{+2} *or* Co^{III} *with* $\alpha\beta$ *the same precipitate is probably obtained in all five titrations.* The error, too, is of approximately the same order and amounts to a few tenths of a microgram per ml.

Titrations of $Na_3Co^{III}(NO_2)_6$ *with α-nitroso-β-naphthol in alcoholic solutions*

Table IV gives the composition and results of such titrations. Comparing the results of experiments 1 and 2 with those of 3 and 4, we see that (exactly as

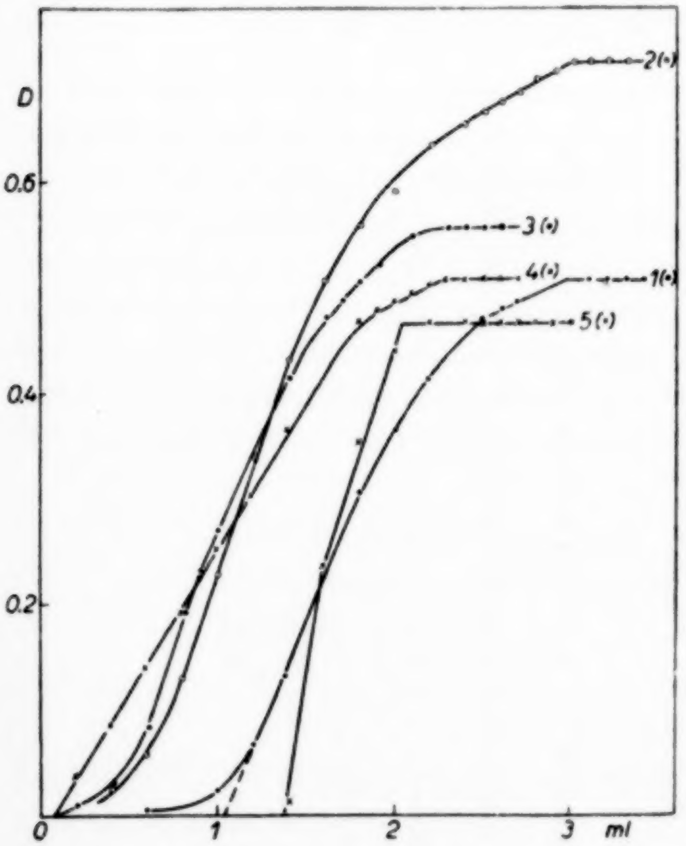

Fig. 3. Titrations of $Co(NO_3)_2$ or $Na_3Co(NO_2)_6$ solutions with α-nitroso-β-naphthol (in 50% acetic acid).

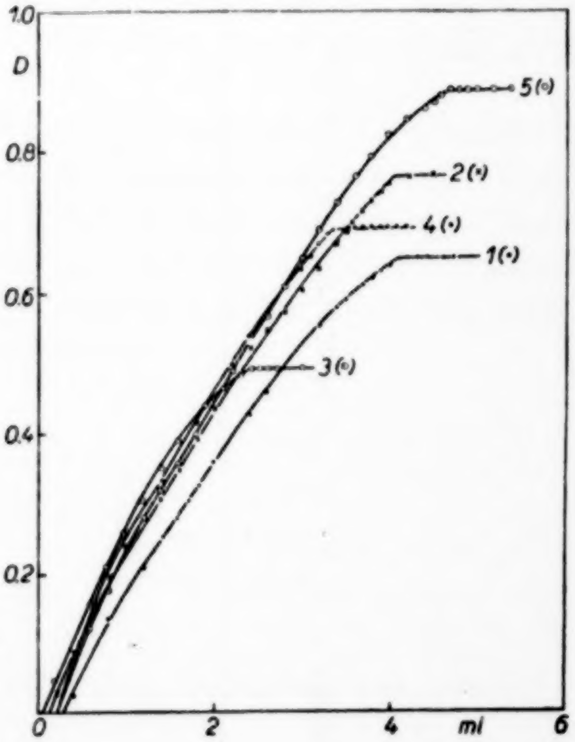

Fig. 4. Titrations of $Na_3Co(NO_2)_6$ solutions with α-nitroso-β-naphthol, in alcohol.

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TABLE III

Composition: 20 ml solution + x ml $\alpha\beta$ (50% acetic acid) 0.005M. Temp. 20° (± 0.1°) Red filter

Exp. number	Solution	mg Co	x ml		Initial precip. at ml	Max. density	Approx. titration time in min.	Error			found: $\frac{[\alpha\beta]}{[Co]}$
			content	found				%	γ	γ/ml	
1	5 ml $Co(NO_3)_2$ 0.001M + 4 ml Na-acetate M + 1 ml CH_3COOH conc. + 10 ml H_2O	0.29	4.0	4.10	0.4	0.65	41	+2.5	7.3	0.4	4.1
2	5 ml $Co(NO_3)_2$ + 0.001M + 4 ml Na-acetate M + 11 ml H_2O	0.29	4.0	4.08	0.0	0.76	20	+2.0	5.8	0.3	4.1
3	4 ,, $Na_3Co(NO_3)_6$ 0.001M + 2 ml Na-acetate M + 14 ml H_2O	0.24	2.30	2.32	0.0	0.49	13	+0.9	2.2	0.1	2.9
4	6 ,, ,, 0.001 ,, + 2 ,, ,, ,, + 12 ,, ,,	0.35	3.45	3.43	0.0	0.69	29	+0.6	2.1	0.1	2.9
5	8 ,, ,, 0.001 ,, + 2 ,, ,, ,, + 10 ,, ,,	0.47	4.61	4.70	0.0	0.88	40	+1.9	8.9	0.45	2.9

was the case with similar titrations of cobaltous with $\alpha\beta$), the sensitivity of Co^{III} is three times as great in a 50% alcoholic solution as in a water solution. In all cases the first maximum point lies at the molar ratio of 1 Co : 3 $\alpha\beta$ with an error between zero and 1.3%. The results of experiments 5 and 6, with citrate or tartrate dissolved in 50% alcoholic solutions, are most instructive. In the citrate solution no precipitation whatever occurs, while in the tartrate solution the *initial* precipitation occurs very late and very near to the first maximum point. This is probably due to the low concentration of cobalt. In spite of this *we obtain, in the presence of tartrate, the first maximum point at the molar ratio of 1 Co : 2 $\alpha\beta$* with an error of 1%. *Exactly the same molar ratio is obtained in the presence of Co^{+2} under similar working conditions* (see Table II). In both cases, *all* the α-nitroso-β-naphthol which was added, is used *solely* for the formation of $Co^{II}(\alpha\beta)_2$ with or without the participation of tartrate in the compound obtained.

On comparing exp. 4 (Table II) with exp. 6 (Table IV) we establish the fact that the points of initial precipitation are in agreement, giving the *same* value of solubility in both cases. This is a further indication that the same compound is obtained in both cases.

Gravimetric determinations of the precipitates

Gravimetric determinations of some of the precipitates were made. The working conditions and the compositions were, as far as possible, identical to those used during the heterometric titrations.

Known quantities of $Co(NO_3)_2$(or $Na_3Co^{III}(NO_2)_6$) dissolved in 50% alcohol, were precipitated by the dropwise addition of alcoholic solutions of 0.02*M* α-nitroso-β-naphthol. The total amount of $\alpha\beta$ added in each case was more than four times the amount of cobalt present. The precipitates were repeatedly washed with 50% alcohol and then dried at 130° until constant weight was obtained. We present here an example of such a determination:

Cobalt content calculated as $Co(\alpha\beta)_3$	= 0.2893 g
First weighing of the precipitate	= 0.3087 ,,
Second ,, ,, ,, ,,	= 0.3057 ,,
Third ,, ,, ,, ,,	= 0.3048 ,,

Calculated as $Co(\alpha\beta)_3$, the average error of such determinations was equal to ∼5%.

Unfortunately, the precipitation of Co^{III} from $Na_3Co^{III}(NO_2)_6$, under conditions similar to those of the previous experiments, gave precipitates that were too fine to be filtered without loss.

TABLE IV

Composition: 5 ml $Na_3Co(NO_2)_6$ aM + 15 ml supplement + x ml α-nitroso-β-naphthol bM alc. Temp. = 20° (± 0.1°) Red filter

Exp. number	Supplement	mg Co	Molarity of		x ml		Initial prec. at ml	Max. density	App. titr. time in min.	Error			$\frac{[\alpha\beta]}{[Co]}$
			$\alpha\beta$	Co	content	found				%	γ	γ/ml	
1	1 ml CH_3COOH M + 4 ml H_2O + 10 ml alcohol	0.15	0.0025	0.0005	3.0	2.96	1.0	0.51	18	—1.3	—2.0	—0.1	3:1
2	1 ,, ,, ,, + 1 ,, Na-acetate M + 3 ml H_2O + 10 ml alc.	0.15	0.0025	0.0005	3.0	3.0	∾0.3	0.72	20	0.0	0.0	0.0	3:1
3	1 ,, ,, ,, + 14 ,, H_2O	0.44	0.01	0.0015	2.25	2.22	0.4	0.56	15	—1.3	—5.7	—0.3	3:1
4	1 ,, ,, ,, + 1 ,, Na-acetate M + 13 ml H_2O	0.44	0.01	0.0015	2.25	2.26	0.0	0.51	13	0.5	2.2	0.1	3:1
5	1 ,, ,, ,, + 3 ,, H_2O + 10 ml alcohol + 1 ml Na_3-citrate M	0.15	0.0025	0.0005			> 3.5	0.0	7				
6	1 ,, ,, ,, + 3 ,, H_2O + 10 ml alcohol + 1 ml Na_3-tartrate M	0.15	0.0025	0.0005	3.0	2.02	1.4	0.47	19	32.7			2:1

DISCUSSION

The experiments and the results which are presented in this paper may serve two purposes. They may be used to reach an understanding of the different reactions which occur on a quantitative basis, under different working conditions, between cobalt and α-nitroso-β-naphthol. Secondly, they may be used to give the conditions which are necessary for a precise micro and submicro heterometric determination of either cobalt with $\alpha\beta$ or *vice versa*.

In all cases, well-defined critical optical density end-points are obtained which coincide with the end of the reaction and the quantitative formation of a cobalt-$\alpha\beta$ precipitate. Cobalt(II), when titrated with $\alpha\beta$ gave quantitatively in acid solutions, precipitates at the molar ratio of 1 Co : 4 $\alpha\beta$. Under similar working conditions, $Na_3Co^{III}(NO_2)_6$ precipitated with $\alpha\beta$ gave the ratio 1 Co : 3 $\alpha\beta$. It is interesting to note that a given amount of cobalt, either as Co^{II} or Co^{III}, if precipitated with $\alpha\beta$ from an alcoholic solution, gives the same maximum density *value*. This leads us to the assumption that in both cases (Co^{II} or Co^{III}) the same compound may be obtained. The gravimetric determination of the *washed* precipitate (which was obtained with Co^{II}) indicates that the precipitate obtained at the ratio 1 Co : 4 $\alpha\beta$ may actually have the composition $Co(\alpha\beta)_3$. Logically, we come to the conclusion that when only the same amount of cobalt is analysed, the maximum density *value* of $[Co(\alpha\beta)_3]$ is *independent* of the valency state of cobalt and also independent of the molar ratio at the critical end-point. If we assume that the cobalt in the precipitate is in the trivalent state, then the stoichiometric reactions between Co^{II} and $\alpha\beta$ would have to be presented in the following way:

$$Co^{+2} + \alpha\beta \rightarrow Co^{+3} + \alpha'\beta' \text{ (or } \overline{\alpha\beta}\text{)}, \quad (1)$$

$$Co^{+3} + 3\alpha\beta \rightarrow Co(\alpha\beta)_3 \downarrow \quad (2)$$

In the case of $Na_3Co^{III}(NO_2)_6$, only reaction (2) would take place. From our experiments we see that the two reactions proceed *quantitatively* both in 65% alcoholic solution and in 50% acetic acid solution. In favour of reaction (1) is the fact that in most stable complex compounds of cobalt, the latter is in the *tri*valent state. These explanations only support the view already accepted by ILINSKI and others.

Unfortunately, there are serious objections to the trivalency of cobalt in the $\alpha\beta$ complex. It is difficult to believe that in 65% alcohol or in 50% acetic acid solutions the *oxidation* (1) goes smoothly and quantitatively. In addition, we find that in the concentrated alcoholic tartrate solution both Co^{II} and $Na_3Co^{III}(NO_2)_6$ give *quantitatively* the same compound $Co(\alpha\beta)_2 \downarrow$.

Summarizing the heterometric results we find three different molar ratios which are obtained at the critical maximum density points. They are: 1 Co : 4 $\alpha\beta$, 1 Co : 3 $\alpha\beta$ and 1 Co : 2 $\alpha\beta$. The ratio 1 Co : 4 $\alpha\beta$ is obtained only with Co^{II}; the ratio 1 Co : 3 $\alpha\beta$ is obtained with $Na_3Co^{III}(NO_2)_6$ and the ratio 1 Co : 2 $\alpha\beta$ is obtained in the alcoholic tartrate solution both with Co^{II} and Co^{III}.

In all three cases, the maximum optical density values obtained are apparently independent of the valency state of cobalt and the ratios at the critical point found *when* the same amount of cobalt is determined. All three ratios may be used for the quantitative determination of cobalt with the same accuracy.

CONCLUSIONS

Composition

1. Co when titrated with α-nitroso-β-naphthol (in alcohol or 50% acetic acid) heterometrically in neutral or acidic solution, gives a first maximum density point exactly at the molar ratio of 1[Co] : 4[$\alpha\beta$]. If $Na_3Co^{III}(NO_2)_6$ is used instead, this ratio is exactly 1[Co] : 3[$\alpha\beta$].

2. Co^{II} or Co^{III}, if dissolved in an alcoholic solution (50%) which contains Na_2-tartrate in large excesses, gives the first maximum density point exactly at the ratio 1[Co] : 2[$\alpha\beta$].

3. With the same amount of cobalt present in the solution, the maximum density values which are obtained at 1[Co] : 4[$\alpha\beta$] and 1[Co] : 3[$\alpha\beta$] are *identical* notwithstanding the different amount of α-nitroso-β-naphthol used for the titration.

4. The optical density which was obtained with Co^{II} in the presence of a large excess of sodium tartrate, at the ratio of 1[Co] : 2[$\alpha\beta$], was of the same order of magnitude as before, using the same quantity of cobalt.

5. It is assumed that the insoluble Co-α-nitroso-β-naphthol compound, which is obtained either at the ratio 1 : 4 or 1 : 3 is identical.

Complexing agents

6. Trisodium citrate has no influence on the precipitation of cobalt in acetic acid-water or acetic acid-alcohol solutions. Disodium tartrate has no influence on the precipitation of cobalt in acetic acid-water solution.

7. The presence of ethylenediaminetetraacetic acid prevents the precipitation of cobalt(II) with α-nitroso-β-naphthol from alkaline, neutral or acidic solutions. On the other hand, no dissolution of the insoluble cobalt-α-nitroso-β-naphthol occurs if titrated with an Na_2-EDTA solution. The density values of cobalt-α-nitroso-β-naphthol suspensions, once precipitated, are not influenced by the addition of EDTA during the titration.

Analysis

8. Cobalt solutions of 0.0001M-0.0005M (or 0.15-0.5 mg cobalt in 20 ml) can be determined heterometrically with α-nitroso-β-naphthol, with an error of 0-3%. The α-nitroso-β-naphthol may be dissolved either in 50% acetic or alcoholic solution. An alcoholic solution is preferable.

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9. The sensitivity of the cobalt determination is almost threefold in a 50% alcoholic solution of cobalt as against a water solution. In addition, the titration time is also reduced in the former case.

10. Solutions of α-nitroso-β-naphthol can be determined with the same accuracy as mentioned before by the titration with a solution of $Co(NO_3)_2$.

Determination of cobalt

Method. In the following two cases the first critical maximum point lies, if cobalt*ous* cobalt is analysed, at the molar ratio of 1[Co] : 4[αβ]. If cobalt*ic* cobalt is used, this ratio lies at 1[Co] : 3[αβ].

1. 20 ml of a *water* solution of cobalt, which contains 0.2-0.5 mg cobalt and 1 ml *M* acetic acid are titrated heterometrically with an alcoholic solution of $\leq$ 0.01*M* α-nitroso-β-naphthol. The titration time is about 20-40 minutes and the error is 0-3%.

2. The titration is carried out in 50% *alcoholic* solution of cobalt. 20 ml solution, which contains about 0.2 mg cobalt, are acidified with acetic acid (1 ml *M* acetic acid) and titrated heterometrically with an alcoholic $\gtrless$ 0.003*M* α-nitroso-β-naphthol solution. The titration time is about 15 minutes and the error is 0-3%.

Determination of α-nitroso-β-naphthol

3. 20 ml of an alcoholic (50%-60%) solution of $\gtrless$0.001*M* α-nitroso-β-naphthol which is acidified with acetic acid (1 ml *M* acetic acid), is titrated with a freshly prepared water solution of 0.001-0.002*M* cobalt(II) nitrate. The titration time is about 20 minutes. Error 0-2%. The critical *first* maximum density point lies exactly at the molar ratio of 1[Co] : 4[αβ].

SUMMARY

1. The reaction between cobaltous or cobaltic and α-nitroso-β-naphthol was extensively studied heterometrically both in water and in alcoholic solutions. The influence of complexing agents and of the acidity on the precipitation of cobalt-α-nitroso-β-naphthol was investigated. In all cases the molar ratios: [Co] [αβ] at the end of the precipitation were established and the possible compounds which were obtained were discussed.

2. Micro-analytical heterometric methods are given for the determination of cobalt or α-nitroso-β-naphthol. The determination can be carried out with precision even in concentrations as low as 0.0001*M* Co. Conversely, very dilute alcoholic solutions of α-nitroso-β-naphthol may be titrated with precision with a dilute solution of cobalt nitrate. 0.2-0.5 mg cobalt in 20 ml solution are required for the analysis. The error lies between zero and 3%.

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RÉSUMÉ

1. Le dosage hétérométrique du cobalt par l'α-nitroso-β-naphtol a été appliqué à l'analyse dans l'eau et dans l'alcool. L'influence du réactif complexant et de l'acidité sur la précipitation du cobalt a été étudiée. Les relations moléculaires à la fin de la précipitation [Co] : [$\alpha\beta$] ont été déterminées.

2. Des microméthodes hétérométriques sont proposées pour la détermination du cobalt par l'α-nitroso-β-naphtol. La détermination peut être effectuée avec précision jusqu'à des concentrations 0.0001M en cobalt. Des solutions alcooliques très diluées en α-nitroso-β-naphtol peuvent être titrées avec précision par une solution diluée de nitrate de cobalt. 0.2-0.5 mg de cobalt dans 20 ml de solution sont nécessaires pour l'analyse. L'erreur varie entre 0 et 3%.

ZUSAMMENFASSUNG

1. Die heterometrische Bestimmung von Kobalt mit α-Nitroso-β-naphtol wurde für Analysen in Wasser und in Alkohol angewendet. Der Einfluss des komplexierenden Reaktives und der Säurekonzentration auf Ausfällung des Kobalts ist untersucht worden. Die Molekularverhältnisse am Ende der Ausfällung, [Co] : [$\alpha\beta$] sind bestimmt worden.

2. Die heterometrische Mikromethode wird für die Bestimmung des Kobalts mit α-Nitroso-β-naphtol vorgeschlagen. Die Bestimmung kann mit Präzision bis zu Konzentrationen von 0.0001M Kobalt ausgeführt werden. Die sehr verdünnten alkoholischen Lösungen von α-Nitroso-β-naphtol können mit Genauigkeit mit einer verdünnten Kobaltnitratlösung titriert werden. 0.2-0.5 mg Kobalt in 20 ml Lösung sind für die Analyse notwendig. Der Fehler variiert zwischen 0 und 3%.

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HETEROMETRIC MICRO-DETERMINATION OF COBALT WITH α-NITROSO-β-NAPHTHOL IN THE PRESENCE OF FOREIGN METAL

by

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The reaction of cobalt with α-nitroso-β-naphthol (= "$\alpha\beta$") and its analytical application was studied extensively in the previous report[1]. In this paper we present some of the results which were obtained of an analysis of cobalt in the presence of foreign metals. The determinations were carried out in three media (this is based on the experience previously gained): (a) in acetic acid 50% alcoholic solution; (b) in aqueous acetic acid solution, and (c) in the presence of Na_3-citrate acting as metal binder. Some parallel heterometric titrations were made with the trivalent cobalt. In the alcoholic solutions the sensitivity of the heterometric determination is greater than in aqueous solutions. For a given amount of cobalt, the values of the maximum density were hardly influenced by the presence of foreign metals. They were also independent of the valency state of cobalt. The amount of cobalt required for an analysis was between 0.15 mg and 0.45 mg cobalt in 20 ml solution (concentration $\geqslant 1 \cdot 10^{-4} M$). The errors were between zero and 3%. No obvious relationship seems to exist between the amount of cobalt used and the magnitude of the error.

EXPERIMENTAL

The same technique and the same apparatus were used as described in the previous paper. All the chemicals were either analytical reagents or chemically pure reagents. The results are independent of the room temperature. In spite of this, all titrations were carried out at a constant temperature of 20° C (± 0.1°). Since the maximum density *values* are dependent on the room temperature, they may best be compared if the titrations are carried out at a constant temperature.

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[1] M. BOBTELSKY AND E. JUNGREIS, *Anal. Chim. Acta*, 12 (1955) 248.

TABLE I

Composition: 5 ml $Co(NO_3)_2$ aM + 15 ml supplement + x ml α-nitroso-β-naphthol bM alc.

Exp. number	Supplements	% Co
1	1 ml CH_3COOH M + 3 ml H_2O + 1 ml $MgSO_4$ M + 10 ml alc.	0.62
2	1 ,, ,, ,, + 3 ,, ,, + 1 ,, $Ca(NO_3)_2$ M + 10 ml alc.	0.37
3	1 ,, ,, ,, + 3 ,, ,, + 1 ,, $BaCl_2$ M + 10 ml alc.	0.11
4	1 ,, ,, ,, + 3 ,, ,, + 1 ,, $Zn(NO_3)_2$ M + 10 ml alc.	0.22
5	1 ,, ,, ,, + 3 ,, ,, + 1 ,, $NiCl_2$ 0.1M + 10 ml alc.	2.6
6	1 ,, ,, ,, + 1 ,, Na_3-citrate M + 1 ml $MnCl_2$ 0.5M + 12 ml H_2O	1.6
7	1 ,, ,, ,, + 1 ,, ,, ,, + 1 ,, $Pb(NO_3)_2$ 0.1M + 12 ,, ,,	2.1
8	1 ,, ,, ,, + 1 ,, ,, ,, + 1 ,, $CuSO_4$ 0.1 ,, + 12 ,, ,,	6.5
9	1 ,, ,, ,, + 1 ,, ,, ,, + 1 ,, $Cr(NO_3)_3$ 0.5 ,, + 12 ,, ,,	1.66
10	1 ,, ,, ,, + 1 ,, ,, ,, + 1 ,, $AlCl_3$ 0.5 ,, + 12 ,, ,,	3.26
11	1 ,, ,, ,, + 1 ,, $Pb(NO_3)_2$,, + 13 ,, ,,	0.21
12	1 ,, ,, ,, + 1 ,, $Ni(NO_3)_2$ 0.5M + 13 ,, ,,	1.48
13	1 ,, ,, ,, + 1 ml Na_3-Citrate M + 1 ,, ,, 0.5 ,, + 12 ,, ,,	1.48
14	1 ,, ,, ,, + 1 ,, ,, ,, + 1 ,, ,, 0.1 ,, + 12 ,, ,,	7.5
15	1 ,, ,, ,, + 1 ,, $AlCl_3$ M + 13 ,, ,,	1.06
16	1 ,, ,, ,, + 1 ,, $Cr(NO_3)_2$ M + 13 ,, ,,	0.55
17	1 ,, ,, ,, +1 ,, $CdSO_4$ M + 13 ,, ,,	0.26
18	1 ,, ,, ,, + 1 ml Na_3-citrate M or 1 ,, Na_2-tartrate M + 1 ml $FeCl_3$ 0.1M + 12 ,, ,,	5.0
19	1 ,, Na-acetate M + 1 ml $Ni(NO_3)_2$ 0.1M + 13 ml H_2O	7.5
20	1 ,, CH_3COOH M + 1 inl $Pb(NO_3)_2$ M + 13 ml H_2O	0.14
21	1 ,, ,, ,, + 1 ,, $ZnSO_4$,, + 13 ,, ,,	0.44

Temp. 20 (± 0.1)°. Red filter.

Molarity of		Co content in mg	x ml		Initial precip. at min.	Max. density	Approx. titrat. time in min.	Error		
$\alpha\beta$	Co		content	found				%	γ	γ/ml
0.0033	0.0005	0.15	3.0	3.06	0.8	0.70	22	+2.0	+3.0	+0.2
0.0033	0.0005	0.15	3.0	3.00	1.0	0.65	26	0.0	0.0	0.0
0.0033	0.0005	0.15	3.0	3.10	0.8	0.63	26	+3.3	+5.0	+0.3
0.0033	0.0005	0.15	3.0	2.98	1.0	0.63	23	—0.7	—1.1	—0.1
0.0033	0.0005	0.15	3.0		>3.5	0.0				
0.01	0.0015	0.44	3.0	3.08	0.2	0.91	15	2.7	4.0	0.2
0.01	0.0015	0.44	3.0	3.02	0.2	0.92	20	+0.7	+3.1	+0.2
0.01	0.0015	0.44	3.0	>3.5	0.0	∞0.77	10			
0.01	0.0015	0.44	3.0	3.0	0.2	0.87	19	0.0	0.0	0.0
0.01	0.0015	0.44	3.0	3.12	0.3	0.84	14	+4.0	+17.6	+0.9
0.01	0.0015	0.44	3.0	3.03	0.4	0.89	18	+1.0	+4.4	+0.2
0.01	0.0015	0.44	3.0	>3.5	0.4	∞0.90				
0.01	0.0015	0.44	3.0	>3.5	0.4	∞0.97	33			
0.01	0.0015	0.44	3.0	3.06	0.2	0.84	23	+2.0	+ 8.8	+0.4
0.01	0.001	0.29	2.0	2.04	0.0	0.84	55	+2.0	+ 5.8	+0.3
0.01	0.001	0.29	2.0	2.04	0.4	0.46	40	+2.0	+ 5.8	+0.3
0.01	0.0015	0.44	2.0	2.04	0.2	0.64	60	+2.0	+5.8	+0.3
0.01	0.001	0.29		∞						
0.01	0.0015	0.44	3.0	>3.5		0.08				
0.01	0.001	0.29	2.0	1.95	0.0	0.68	55	—2.6	—7.5	—0.4
0.01	0.001	0.29	2.0	2.04	0.4	0.64	40	+2.0	+5.8	+0.3

RESULTS

Titrations in alcoholic solutions

Table I and Fig. 1 (the same numbers are used), experiment 1-5, give results of some of the titrations of cobaltous in 50% alcoholic solutions. Although these solutions contained more than 99% foreign metals, a minimum amount of cobalt was used for the titrations; the same minimum was used in the absence of foreign metals. The errors are between zero and 3%. The highest error was obtained in the presence of barium (0.1% Co). The initial precipitation occurs only upon the addition of *one third* of the $\alpha\beta$ necessary for a complete titration. Consequently, this approaches very near to the lower limit of cobalt concentration which may be used for a heterometric determination of cobalt. As experiment 5 shows no precipitation of cobalt occurs in a nickel solution of 97.4% nickel. The remaining titrations of Table I were all carried out in aqueous solution. Some experiments with $Na_3Co^{III}(NO_2)_6$ in 50% alcohol are given in Table II and Fig. 2. (the same numbers are used). While in all cases with cobaltous cobalt, the molar ratio at the critical point was 1 Co : 4 $\alpha\beta$, with $Na_3Co^{III}(NO_2)_6$ the ratio 1 Co : 3 $\alpha\beta$ was obtained. The presence of large excesses (>99%) of foreign metals has therefore no appreciable influence on these ratios. On the other hand, the sensitivity of the Co-$\alpha\beta$ reaction is independent of the valency state of the cobalt which was used for the titration. It is remarkable that the points of *initial* precipitation in titrations with $Na_3Co^{III}(NO_2)_6$, in the presence of Mg or Zn, lie extremely near to the end of the titration. This requires further study.

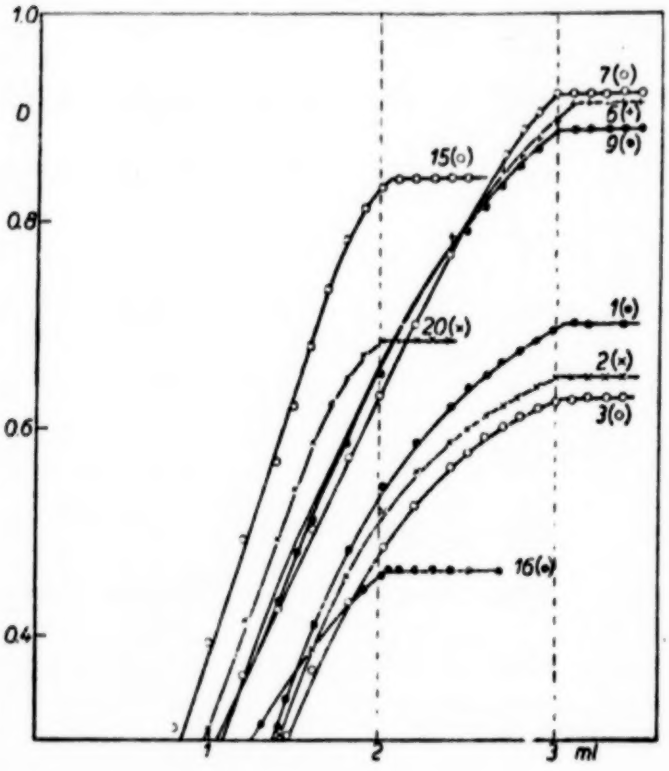

Fig. 1. Titration curves of cobalt with α-nitroso-β-naphthol in the presence of foreign metals.

Titrations in aqueous solutions

Most of the titrations were carried out in weak acetic acid solutions, some in the presence and some in the absence of Na_3-citrate (Table I, exps. 6-21 and Fig. 1). No maximum density value was obtained in the presence of nickel at the calcu-

TABLE II

Composition: 5 ml $Na_3Co^{III}(NO_2)_6$a*M* + 15 ml supplement + x ml α-nitroso-β-naphthol b*M* alc. Temp. = 20° (± 0.1°). Red filter

Exper. number	Supplement	Mg Co	% Co	Molarity of		*x* ml		Initial precip. at min.	Max. density	Approx. titration time in min.	Error			$\frac{[\alpha\beta]}{[Co]}$
				αβ	Co	Content found					%	γ	γ/ml	
1	1 ml CH_3COOH *M* + 3 ml H_2O 10 ml acohol 1 ml $MgSO_4$ *M*	0.15	0.62	0.0025	0.0005	3.0	3.0	2.4	0.59	13	0.0	0.0	0.0	3:1
2	1 ml CH_3COOH *M* + 3 ml H_2O 10 ml alcohol 1 ml $BaCl_2$ *M*	0.15	0.11	0.0025	0.0005	3.0	3.0	1.1	0.43	30	0.0	0.0	0.0	3:1
3	1 ml CH_3COOH *M* + 3 ml H_2O 10 ml alcohol 1 ml $Zn(NO_3)_2$ *M*	0.15	0.22	0.0025	0.0005	3.0	2.96	2.5	0.44	15	—1.3	2.0	0.1	3:1
4	1 ml CH_3COOH *M* + 3 ml H_2O 10 ml alcohol 1 ml $Ca(No_3)_2$ *M*	0.15	0.37	0.0025	0.0005	3.0	3.05	1.0	0.69	19	1.7	2.6	0.1	3:1

lated end-point of the titration: the optical density rose continously. In a 92.5% nickel solution, cobalt could be determined only in the presence of citrate (exp. 14). The error was 2%. The density rose continuously in the presence of iron, even with citrate or tartrate present (exp. 18). In solutions of chromium or aluminium (∿99%), cobalt could be determined without difficulty (better in the absence of citrate). In the presence of chromium, a higher density value is obtained with citrate present. The titration time is also reduced in the presence of citrate. In zinc (0.44% Co) or Cd (0.26% Co) solutions, the determination could be made with an error of 2% (compare Table 1, exp. 4). In the presence of copper, the density values rose above the calculated end-point (exp. 8). The determination could be made in a manganese solution (exp. 6), (an alcoholic solution may also be used). In lead solutions, traces of cobalt (0.1% Co) could be determined (exp. 20) in the absence of citrate.

A series of experiments were made in the presence of trisodium-citrate and nickel chloride or nickel nitrate in order to increase the quantity of nickel in solution above that which was used in experiment 14 (Table I). Neither in the presence nor absence of acetic acid (or NH_3) could a definite maximum point be obtained and the densities rose continuously after the calculated point had been reached. When copper was added the density kept increasing even after the calculated point for the amount of cobalt present. Although no special titrations with mixtures of three or more cations were made, it may be assumed that no special difficulties would arise if the behaviour of the components is taken into account.

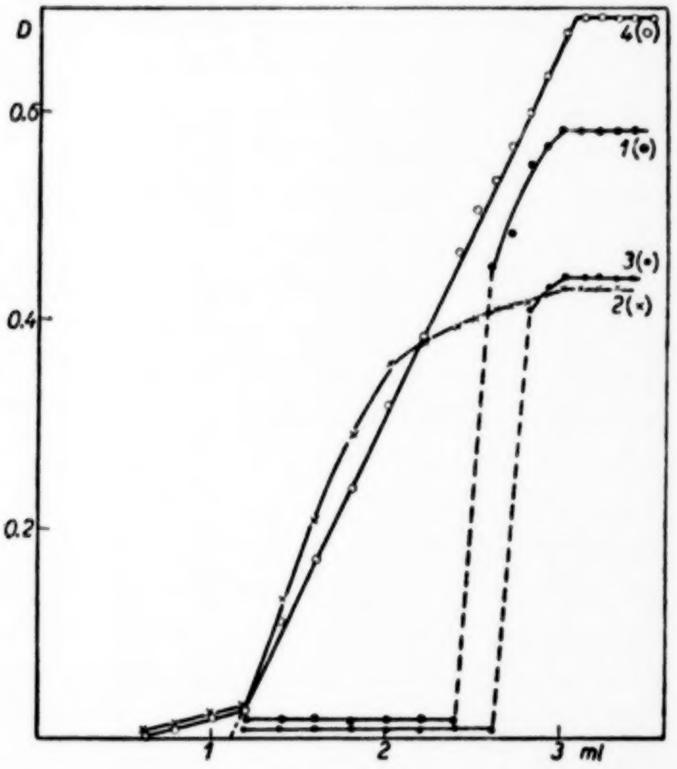

Fig. 2. Titration curves of $Na_3Co(NO_2)_6$ with α-nitroso-β-naphthol in the presence of foreign cations.

CONCLUSIONS

From the previous results, it can be seen that the analysis of cobalt (between one-tenth and a few percent) may be carried out in the presence of foreign metals either in water or 50% alcoholic solutions. In both cases the solution must be acidified with acetic acid.

Influence of alcohol: The sensitivity is higher in the presence of alcohol. If trisodium citrate is added, only a water solution can be used as the solubility of alkali citrate is reduced in alcohol.

Influence of trisodium citrate: The titration time is generally reduced in the presence of citrate. In the presence of some foreign metals the addition of citrate is essential for the analysis.

In the presence of aluminium or chromium ($\overset{\sim}{<}$ 1% Co)*:* The analysis is best carried out in the absence of citrate, but can be carried out even in an excess of citrate.

In the presence of lead: Solutions which contain only tenths of a percent of cobalt are analysed in the absence of citrate. If the cobalt amounts to a few percent, then the use of a citrate solution (in excess) is to be preferred.

In the presence of cadmium: The water solution is analysed in the absence of citrate.

In the presence of zinc: (< *1*% cobalt) Either water or alcoholic solution may be used. No citrate is necessary.

In the presence of nickel: The amount of cobalt must not be less than $\sim$10%. The determination can be made only in the presence of excess citrate.

In the presence of barium: The cobalt may amount to 0.1%.

In the presence of calcium or magnesium: The cobalt may be less than 1%.

METHOD

General

A rough titration is best made first. The final titration is then made, adding the α-nitroso-β-naphthol solution drop by drop and stirring vigorously and continuously. Careful readings are made towards the end. The readings on the galvanometer become constant in a period between a few seconds and 1-2 minutes. The first maximum density point is determined by the intersection of the constant maximum density line with the last part of the heterometric titration curve. It is advisable to analyse solutions which contain sufficient cobalt and give the initial precipitation near the beginning. In all cases the error amounts to 0-3%.

Procedure

20 ml solution (including 1 ml M CH_3COOH and trisodium citrate if present) which contains 0.2-0.5 mg cobalt and more than 90% foreign metal, is titrated heterometrically with an alcoholic solution of 0.0033M-0.01M α-nitroso-β-naphthol.

SUMMARY

A heterometric method is presented for the determination of cobalt in solutions of other metals. The cobalt comprises 0.1—3% of the total metal content. The amount of cobalt determined is 0.2-0.5 mg in 20 ml of solution. The titration generally takes 10-20 minutes at room temperature, and the error is 0-3%.

RÉSUMÉ

Une méthode hétérométrique est proposée pour la détermination du cobalt en présence d'autres métaux. La teneur en cobalt est de 0.1-3%. La quantité de cobalt déterminée est de 0.2-0.5 mg/20 ml. La titration dure environ 10-20 minutes à la température ordinaire et l'erreur est de 0-3%.

ZUSAMMENFASSUNG

Eine heterometrische Methode zur Bestimmung von Cobalt in Lösungen von anderen Metallen wird beschrieben. Das Cobalt macht 0.1%-3% von dem Totalgehalt an Metall aus. 0.2-0.5 mg Cobalt in 20 ml Lösung wird bestimmt. Die Titration dauert bei gewöhnlicher Temperatur 10-20 Minuten. Fehler 0-3%.

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CACOTHELINE AS A REAGENT FOR THE DETECTION OF FERROUS AND FERRIC IRON

by

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Cacotheline is a yellow powder obtained by the nitration of brucine. LEUCHS AND LEUCHS[1] appear to have been the first to notice that stannous salts produce a characteristic amethyst colour with cacotheline. LEUCHS, OSTERBURGAND KAEHRN[2] and LEUCHS, WINKLER AND LEUCHS[3] reported that reducing anions such as sulphide, sulphite, bisulphite and thiosulphate also reduce cacotheline to a red-coloured compound under suitable conditions. GUTZEIT[4] proposed this colour reaction as a sensitive test for stannous tin. FEIGL[5] stated that the test is more sensitive when carried out as a spot test rather than in a test tube. He gave the limit of identification as 0.2 γ tin and the concentration limit as 1:250,000. NEWELL and co-workers[6] carried out a somewhat detailed investigation on the sensitivity of this test and the interference of various ions in carrying out the test for stannous tin. They found that Sb^{+3} salts also give the test but only at concentrations higher than 10^{-2} molar. ROSENTHALER[7] stated that a colour similar to that given by Sn^{+2} is also given by Ti^{+2}, U^{+3}, Rh^{+3}, the lower oxides of Mo, W, and Cb. The test is also given by ferrous sulphate, in the presence of phosphoric acid or fluoride but not in their absence. FEIGL[8] used cacotheline as a spot test reagent for trivalent vanadium. The limit of identification is set at 2 γ vanadium and the concentration limit at 1 : 25,000. Despite these interferences, cacŏtheline is frequently employed for the detection of tin. NECHAMKIN AND SANDERS[9] used cacotheline for the detection of tin in metal coatings. ROSSI AND SERANTES[10] used cacotheline for the detection of tin in alloys of tin, lead and bismuth. FLOOD AND SMEDSAS used the same reagent for the detection of tin in chromatographic analysis. KUCHMENT AND GENGRINOVICH[12] used cacotheline as an indicator for the titration of a hot ferric chloride solution with stannous chloride.

It is evident from the foregoing that cacotheline has been used widely as a reagent for stannous tin, but so far it has not been used for the detection of ferrous and ferric iron. It is the object of the present investigation to see how far cacotheline serves as a reagent for the detection of ferrous and ferric iron. Cacotheline is not ordinarily reduced by Fe^{+2} ions. The reduction takes place, however, if fluoride or oxalate ions are added. This may be explained on the basis of the following reaction, which may be assumed to be reversible.

$$Fe^{+2} \rightleftharpoons Fe^{+3} + \theta.$$

Fluoride or oxalate ions are known to form complexes with ferric ions. When there is sufficient concentration of the complexing agent, the concentration of the Fe^{+3} ion is lowered, and thereby its reaction potential is also lowered. Since the above reaction is reversible, we can conclude that the reduction of Fe^{+2} is increased in the presence of the complexing agent. Hence, under such conditions ferrous ions are able to reduce the cacotheline. This provides a significant example of the raising of the reaction potential of the ferrous salt by masking the ferric ion through complex formation.

EXPERIMENTAL

A large number of preliminary experiments has shown that the colour obtained by the action of ferrous iron on cacotheline in the presence of oxalate is either blue, green or pink according to the experimental conditions. It was also noticed that the colours were very unstable. Hence detailed systematic experiments have been carried out to ascertain the optimum conditions of pH, oxalate concentration, cacotheline concentration etc., that would give stable pink colours.

Solutions required: (1) 0.25% cacotheline solution.

(2) 0.01*N* ferrous ammonium sulphate solution containing sulphuric acid at 1.0*N*.

(3) 0.1*N* sodium oxalate solution.

(4) Walpole buffer solutions (Sodium acetate — Hydrochloric acid) ranging from 5.89 pH to 0.65 pH.

5.0 ml of the appropriate buffer solution are placed in a test tube, followed by 0.2 ml of 0.25 % of cacotheline solution, 2.0 ml of decinormal sodium oxalate solution, and 0.5 ml of the ferrous ammonium sulphate solution. The results are recorded in Table I.

From the above results, it will be seen that a good pink colour is obtained when the pH of the solution is varied between 4.58 and 1.42. When the pH of the solution is above 5.20, a blue colour is obtained, whereas at pH 1.24 and below, only a light pink colour is produced and this develops slowly. It will also be noticed that at first the stability of the colour increases as the pH is lowered; but a further decrease of pH below 3.49 results in a decreased stability.

TABLE I

pH	Observation	pH	Observation
5.89	blue colour	3.61	pink, stable for one and half hours
5.55	,, ,,	3.49	pink, stable for one and half hours
5.37	,, ,,		
5.20	bluish pink, stable for 4 minutes	3.09	pink, stable for 30 minutes
4.92	,, ,, stable for 6 minutes	2.72	,, stable for 30 minutes
4.76	,, ,, stable for 8 minutes	2.64	,, stable for 30 minutes
4.58	pink, stable for 10 minutes	1.42	,,
4.39	,, stable for 1 hour	1.24	light pink
4.19	,, stable for 1 hour	1.09	,, ,, after a few seconds
3.95	,, stable for 1 hour	0.75	very pale pink, after several seconds
3.79	,, stable for 1½ hours	0.65	no colour development

Variation of relative proportions of ferrous iron concentration and oxalate concentration

The following experiments were conducted with a Walpole buffer solution of 3.95 pH. 5.0 ml of the buffer solution was placed in a test tube, followed by 0.14 ml of cacotheline solution, X ml of ferrous ammonium sulphate solution and Y ml of sodium oxalate solution.

The observations are recorded in Table II.

TABLE II

X ml of Fe^{+2} salt solution	Y ml of sodium oxalate solution	Colour	Remarks
0.1	0.2	pale pink	fades in 2 min
0.2	0.4	,,	,, ,, 5 ,,
0.3	0.6	,,	,, ,, 10 ,,
0.4	0.8	,,	,, ,, 15 ,,
0.5	1.0	,,	,, ,, 25 ,,
0.6	1.2	,,	,, ,, 40 ,,
0.1	0.4	light pink	,, ,, 10 ,,
0.2	0.8	pink	,, ,, 20 ,,
0.3	1.2	,,	,, ,, 30 ,,
0.4	1.6	,,	,, ,, 40 ,,
0.5	2.0	,,	,, ,, 60 ,,
0.6	2.4	,,	stable for 3 h
0.1	0.8	,,	fades in 20 min
0.2	1.6	,,	,, ,, 25 ,,
0.3	2.4	,,	,, ,, 30 ,,
0.4	3.2	,,	,, ,, 30 ,,
0.5	4.0	,,	,, ,, 40 ,,
0.6	4.8	,,	,, ,, 55 ,,

From the above results, it is seen that a concentration of ferrous iron corresponding to 0.6 ml of 0.01M Fe^{+2} salt solution will give a pink colour stable for 3 hours, when the oxalate concentration corresponds to 2.4 ml of 0.1N oxalate solution, while the cacotheline solution is taken at 0.14 ml in a total volume of about 10-12 ml. Under these conditions, the oxalate concentration is 40 times the concentration of ferrous ions.

Variation of cacotheline concentration

Experiments were carried out varying cacotheline concentration, but keeping the other conditions constant.

TABLE III

5.0 ml of Buffer solution (3.95 pH) + 0.5 ml of 0.01M Fe^{+2} sclution + 2.0 ml of 0.1M sodium oxalate solution + X ml of 0.25 % cacotheline solution.

X ml volume of cacotheline soln.	Colour	Remarks
0.01	pink	
0.05	intensity increases	
0.08	,, ,,	
0.10	,, ,,	fading begins after one hour
0.13	,, ,,	,, ,, ,, 50 min
0.15	,, ,,	,, ,, ,, 45 ,,
0.18	,, ,,	,, ,, ,, 30 ,,
0.20	,, ,,	,, ,, ,, 25 ,,
0.25	,, ,,	,, ,, ,, 10 ,,
0.30	,, ,,	,, ,, ,, 5 ,,

From these results, it is seen that although the intensity of the colour increases with increasing concentration of cacotheline, yet the stability of the colour diminishes as the cacotheline concentration increases.

Sensitivity

Experiments have been carried out at a pH of 3.95 as well as at a pH of 3.09 with varying amounts of the Fe^{+2}. It has been found that even the amount of ferrous iron present in 0.25 ml of a 0.001M ferrous ammonium sulphate solution could be detected. For this purpose 5 ml of the buffer solution, 0.2 ml of 0.025 % cacotheline solution, 2.0 ml of 0.1M sodium oxalate solution were mixed in a test tube followed by 0.25 ml of 0.001M solution of Fe^{+2} salt. The resulting brown-pink colour is stable for only 15 minutes, after which it fades. When the amount of Fe^{+2} to be detected is small, it is necessary to use a dilute solution of cacotheline.

The limit of concentration is 1 : 40,000 of Fe^{+2}. The limit of identification 1.5 γ.

Interference of various acid radicals

In the following experiments, 5.0 ml of a buffer solution of 3.61 pH, 2.0 ml of 0.1M sodium oxalate solution, X ml of 0.1 % solution of the acid radical and 0.5 ml of 0.01M ferrous sulphate solution were mixed in a test tube and kept for one hour and then 0.2 ml of cacotheline (0.25 %) solution was added. The results are tabulated in Table IV.

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TABLE IV

Interfering agent	Volume	Colour	Stability
Chloride	2.0 ml	pink	colour stable for 3 hours
Bromide	2.0 ,,	,,	,, ,, ,, 3 ,,
Iodide	2.0 ,,	,,	,, ,, ,, 1½ ,,
Chlorate	2.0 ,,	,,	,, ,, ,, 1½ ,,
Persulphate	2.0 ,,	,,	,, ,, ,, 2 ,,
Tungstate	2.0 ,,	,,	,, ,, ,, 50 minutes
Molybdate	2.0 ,,	,,	,, ,, ,, 15 ,,
Bromate	0.2 ,,	no colour	
Iodate	0.3 ,,	,, ,,	
Vanadate	0.5 ,,	,, ,,	
Dichromate	0.3 ,,	,, ,,	
Blank	—		

Effect of metal ions

The effect of Cu^{+2}, Mn^{+2}, Ni^{+2}, Sn^{+2} and Cr^{+3} have been studied. X ml of the metal ion solution, 5.0 ml of 0.1*M* Fe^{+2} solution, 2.0 ml of oxalate solution, 5.0 ml of the buffer solution were mixed, and then treated with 0.2 ml of 0.25 % cacotheline solution. Stannous tin has been found to interfere since it also gives a pink colour with cacotheline. Mn^{+2}, Ni^{+2} and Cr^{+3}, do not interfere with the colour development, even when added in amounts of 2.0 ml of 2.5 % solution. The stability of the colour is, however, much less than in their absence; with Co^{+2} the colour is stable only for 2 minutes. Mn^{+2}, and Cr^{+3} may be present up to 6.0 ml. Ni^{+2} interferes, when present at 3.0 ml and above.

Detection of Fe^{+3}

We have now attempted to detect Fe^{+3} iron after reducing it to the Fe^{+2} condition, before carrying out the cacotheline test. For achieving the reduction of Fe^{+3} to Fe^{+2}, we cannot use many of the common reducing agents, as excess of any of these materials is likely to give the colour reaction with cacotheline by itself. We therefore resorted to a novel method of reducing the ferric salt. It was reported by RAO AND RAO[13] that ferric salts are rapidly and quantitatively reduced in sunlight in the presence of excess of sodium oxalate. We found that this reduction takes place even in dilute solutions of the order of 0.001*M*. 1.0 ml of the 0.001*M* solution of the ferric salt is mixed with 2.0 ml of the oxalate solution and 5.0 ml of the buffer solution (3.09 pH) in a glass test tube which is exposed to sunlight for about 15 minutes or to the light from a Philip's Repro lamp for about 30 minutes. The test tube is then brought to the laboratory and treated with 0.2 ml of cacotheline solution (0.025 %). A good pink colour results and is found to be stable for 30 minutes. If the test is carried out on 1.0 ml of 0.01*M* solution, the colour is stable for more than 3 hours. Stannic salts do not interfere in this test, as they are not reduced photochemically by oxalate.

Experiments with complexing agents other than oxalate

The experiments described in the foregoing pages have shown that oxalate serves as an excellent complexing agent for Fe^{+3} ions so that in the presence of oxalate the reaction potential of the system

$$Fe^{+2} \rightleftharpoons Fe^{+3} + (e)$$

is increased consequent to the binding of the Fe^{+3} ions, which may tend to reverse the reaction. It is known that other organic acids like citrate, tartrate, *etc.* also are capable of forming complex ions with Fe^{+3}. Hence experiments have

TABLE V

pH	Sodium malonate M/10	Sodium citrate M/10	Sodium malate M/5	Sodium tartrate *M*	Sodium lactate *M*
5.89	blue color immediately	blue color immediately	light blue	blue	blue
5.57	,,	,,	blue violet	blue violet	light blue
5.37	,,	,,	,,	,,	,,
5.20	,,	dark violet	violet	light violet	v. pale colour
4.92	bluish pink	violet pink	violet	,,	,,
4.76	,,	,,	light pink	light pink	,,
4.58	pink	pink	,,	,,	,,
4.39	,,	,,	,,	,,	,,
3.95	,,	,,	,,	,,	,,
3.79	,,	,,	,,	,,	,,
3.61	,,	,,	,,	,,	,,
3.49	,,	,,	,,	,,	,,
3.29	,,	,,	,,	,,	,,
3.09	,,	,,	,,	,,	,,
2.72	,,	,,	,,	,,	,,
2.62	intensity lower	,,	,,	,,	,,
2.32	,,	,,	,,	,,	,,
1.99	,,	,,	,,	,,	,,
1.85	pink intensity lower	pink	pale pink	light pink	v. pale pink
1.71	,,	,,	,,	,,	,,
1.42	light pink	pink intensity lower	,,	,,	,,
1.24	,,	light pink	pale pink	,,	light pink
1.09	slow development	light pink	no colour	,,	,,
0.91	no colour	no colour	,,	,,	,,
0.75	,,	,,	,,	pale pink	,,
0.65	,,	,,	,,	,,	,,

been carried out using the sodium salts of several organic acids in place of sodium oxalate. A summary of a large number of results is presented in Table V.

5.0 ml of buffer solution + 0.2 ml of 0.25 % cacotheline solution + 2.0 ml of sodium salt solution + 0.5 ml of $0.01M$ Fe^{+2} solution.

The results in the Table V show that citrate and malonate are quite as effective as oxalate, whereas sodium malate, tartrate, and lactate are less effective. The order of effectiveness appears to be

$$\left.\begin{array}{l}\text{Oxalate}\\ \text{Malonate}\\ \text{Citrate}\end{array}\right\} > \text{malate} > \text{tartrate} > \text{lactate}$$

Experiments have also been made with ortho-, pyro- and metaphosphates as complexing agents in place of oxalate. The results are recorded in Table VI.

5.0 ml of buffer + 0.2 ml of 0.25 % cacotheline solution + 1.0 ml of phosphate solution + 0.5 ml of $0.01M$ Fe^{+2} solution.

TABLE VI

pH	Remarks		
	$0.2M$ KH_2PO_4	$0.2M$ $Na_4P_2O_7$	$0.2M$ $NaPO_3$
0.91	no colour	immediate pink; fades in 35 min	pink, stable
1.42	,,	,, ,, ,, ,, 20 ,,	,, ,, ,,
1.99	,,	,, ,, ,, ,, 30 ,,	,, ,, ,,
2.62	,,	,, ,, ,, ,, 15 ,,	,, ,, ,,
3.09	no colour	immediate pink, fades in 15 min	pink; fading begins after 30 min
3.61	,,	,, ,, ,, ,, 10 ,,	light pink, fading begins after 25 min
3.95	,,	,, ,, ,, ,, 10 ,,	,, ,, ,, 25 min
4.39	,,	,, ,, ,, ,, 10 ,,	,, ,, ,, 25 min
4.58	,,	,, ,, ,, ,, 5 ,,	,, ,, ,, 25 min
4.92	,,	,, ,, ,, ,, 3 ,,	,, ,, ,, 25 min

It has been found that orthophosphate does not give the colour, even when added at a volume of 6.0 ml. Comparative experiments with oxalate, pyro- and metaphosphates have shown that oxalate is the most effective followed by pyrophosphate, and metaphosphate. The colours obtained with metaphosphate are, however, more stable then those with pyrophosphate.

SUMMARY

1. Cacotheline has previously been employed as a colorimetric reagent for the detection of Sn^{+2} and V^{+3} ions. The present investigation covers its use as a reagent for the detection of Fe^{+2} and Fe^{+3} ions.

2. Fe^{+2} ions give a pink colour with a solution of cacotheline at a pH lying between 1.48 and 4.58 in the presence of a sufficient concentration of sodium oxalate, which serves to bind the Fe^{+3} ions by complex formation. At a pH below 1.24, only a very light pink colour is produced and this develops slowly. When the pH of the solution is about 5.2, a blue colour is obtained. The limit of identification is 1.5 γ and the concentration limit is 1 : 40,000 of Fe^{+2}. While testing for Fe^{+2} at very low concentration, it is necessary to employ a very dilute solution of cacotheline (0.025 %), while for solutions of higher concentrations saturated cacotheline solution (about 0.25 %) is recommended. A detailed investigation has been made concerning the conditions determining the stability of the pink colour.

3. It has also been observed that sodium malonate, sodium citrate, sodium malate, sodium tartrate and sodium lactate are effective as complexing agents for binding Fe^{+3} ions.

4. Orthophosphate has not been found effective as a complexing agent under the conditions adopted, while pyrophosphate and metaphosphate have been found effective.

5. Fe^{+3} ions are reduced to Fe^{+2} by exposure to sunlight or the light from a Philip's Repro lamp in the presence of the appropriate buffer solution and sodium oxalate.

RÉSUMÉ

1. La cacothéline a déjà été utilisée comme réactif colorimétrique de Sn^{+2} et V^{+3}. Les auteurs se sont proposés de l'appliquer à la recherche des ions Fe^{+2} et Fe^{+3}.

2. Fe^{+2} donne une coloration rose avec la cacothéline à un pH compris entre 1.48 et 4.58, en présence d'une concentration suffisante en oxalate de sodium, permettant de complexer les ions Fe^{+3}. A un pH inférieur à 1.24, il ne se forme que lentement une très faible coloration rouge. A un pH d'environ 5.2, on obtient une coloration bleue. La limite de perceptibilité est de 1.5 et la dilution limite est de 1 : 40.000 Fe^{+2}. Pour déceler de très faibles teneurs en Fe^{+2}, il faut utiliser une solution très diluée de cacothéline (0.025 %), tandis que pour de fortes concentrations, on recommande d'employer 0.25 % environ. Une étude détaillée a été effectuée, pour déterminer les conditions de stabilité de la coloration rouge.

3. Le malonate, le citrate, le malate, le tartrate et le lactate de sodium forment des complexes avec les ions Fe^{+3}.

4. L'orthophosphate n'est pas un agent complexant efficace dans les conditions adoptées, contrairement au pyrophosphate et au métaphosphate.

5. Fe^{+3} est réduit en Fe^{+2} à la lumière solaire ou sous l'action d'une lampe "Philip's Repro" en présence d'une solution tampon appropriée et d'oxalate de sodium.

ZUSAMMENFASSUNG

1. Das Kakothelin wurde schon als kolorimetrisches Reaktiv für Sn^{+2} und V^{+3} verwendet. Die Autoren haben versucht, es auch für die qualitative Analyse von Fe^{+2} und Fe^{+3} anzuwenden.

2. Fe^{+2} gibt mit Kakothelin eine Rosafärbung bei pH-Werten zwischen 1.48 und 4.58 in Gegenwart einer genügend starken Konzentration von Natriumoxalat, welches ermöglicht, Fe^{+3} zu komplexieren. Bei einem pH-Wert unterhalb 1.24

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bildet sich nur langsam eine sehr schwache rote Färbung. Bei einem pH von ungefähr 5.2 entsteht eine blaue Färbung. Die Grenze der Erfassbarkeit liegt bei 1.5 und die Verdünnungsgrenze ist 1 : 40.000 Fe^{+2}. Um sehr kleine Mengen von Fe^{+2} zu ermitteln, verwendet man eine sehr verdünnte Kakothelinlösung (0.025 %), für hohe Konzentrationen dagegen wird ungefähr 0.25 % empfohlen. Eine detaillierte Untersuchung wurde durchgeführt, um die Bedingungen für die Stabilisierung der roten Färbung festzulegen.

3. Das Natrium-malonat, -citrat, -malat, -tartrat und -laktat bilden Komplexe mit Fe^{+3} -Ionen.

4. Das Orthophosphat ist kein wirksames komplexierendes Mittel unter den genannten Bedingungen, im Gegensatz zu Pyrophosphat und Metaphosphat.

5. Fe^{+3} wird reduziert zu Fe^{+2} durch die Wirkung des Sonnenlichtes oder durch Bestrahlung mit einer Lampe ,,Philips' Repro'' in einer geeigneten Pufferlösung und in Anwesenheit von Natriumoxalat.

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ÜBER EINIGE TITRATIONEN NACH DEM „DEAD-STOP" VERFAHREN MIT VERWENDUNG VON QUECKSILBER-ELEKTRODEN

von

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In einem vorigen Artikel[1] wurde die Möglichkeit der Massanalyse nach der „Dead-stop" Methode mit Verwendung zweier Quecksilberelektroden nachgewiesen. Nach Abschluss dieser Untersuchung wurden zwei analoge Durchführungen beschrieben[2,3], wobei zwei Silber-Elektroden verwendet wurden.

Bei den hier beschriebenen Versuchen war vor oder nach, beziehungsweise, vor und nach dem Äquivalenzpunkt ausser dem Grundelektrolyt eine, bei Anwesenheit von metallischem Quecksilber stabile komplexe Quecksilber(II)-verbindung oder ein lösliches Quecksilber(I)-salz (Nitrat oder Perchlorat) vorhanden.

Nachstehend werden sieben Vorschriften für Titrationen, die nach dieser Methode gute Resultate ergeben haben, mitgeteilt. Die elektrische Schaltung wurde bereits früher beschrieben[4].

Bestimmung von Quecksilber(II)

Der Grundelektrolyt enthält per 100 ml 25 ml NaOH 4 *N* und 5 Gramm Na_2SO_3, das sowohl die Lösung sauerstoffrei macht[5] wie auch mit Quecksilber(II)-Ionen einen löslichen Komplex ergibt, der durch das Vorhandensein des Sulfit-Überschusses eine ineinander übergehende anodische und kathodische Welle[6,7] hervorruft, analog dem Quecksilber-Jodomerkurat-System[8]. Die Luft wird aus dem Titriergefäss durch Stickstoff vertrieben und die Lösung wird durch ein Tauchelement auf 50°C erwärmt. Erst dann werden die zwei mit Platinkontakten versehenen Vertiefungen im Boden mit Hilfe eines Hahntrichters mit Kapillarausfluss mit Quecksilber gefüllt. Die zu analysierende Quecksilber(II)-Lösung wird unter Rühren zugesetzt.

Man legt einen Spannungsunterschied von ungefähr 1 mV an, der während des Titrierens beträchtlich grösser wird.

Man lässt nun aus einer Reduktionsbürette[9] Ferrochlorid zufliessen, wodurch die Stromstärke nahezu auf Null absinkt (Fig. 1a).

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Die Reaktionsgleichung ist:

$$Hg(SO_3)_2^{-2} + 2\ Fe(OH)_2 + 2\ OH^- = Hg + 2\ SO_3^{-2} + 2\ Fe(OH)_3.$$

Die Erwärmung ist nicht absolut nötig aber sie erhöht die Reaktionsgeschwindigkeit beträchtlich.

Die Anwesenheit von 5 Gramm KJ hat keinen Einfluss auf diese Titration. Mit einer eingestellten Quecksilber(II)-Lösung ist auf diese Weise die Ermittlung von Dithionit ($S_2O_4^{-2}$) möglich[10].

Chloridbestimmung

Die Basislösung war ungefähr 1*M* $NaNO_3$ und 0.05 — 0.1*N* HNO_3. Sie wurde vor Zugabe des Quecksilbers mit Stickstoff luftfrei gemacht. Danach wurde die zu analysierende Lösung zugesetzt und eine Spannung von etwa 5 mV angelegt. (Diese Reihenfolge wird bei allen Titrationen eingehalten.) Zusatz der Titrierflüssigkeit Quecksilber(I)-nitrat (hergestellt nach BELCHER[11]) oder Quecksilber(I)-perchlorat (hergestellt nach BURRIEL-MARTI[12]) lässt das Galvanometer ausschlagen. Anfänglich erreicht das Galvanometer seinen Endwert sehr träge.

Kurz vor dem Äquivalenzpunkt und danach erfolgt die Einstellung sehr

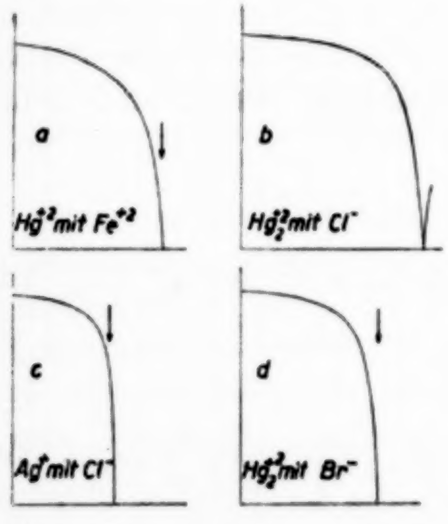

Fig. 1

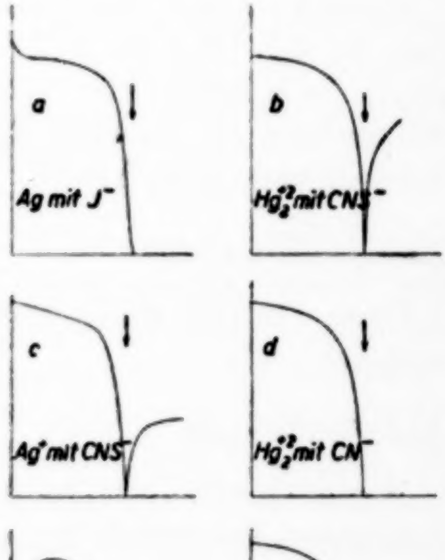

Fig. 2

Ordinate: Skalenteile des Galvanometers
Abscisse: Volumen des Reagenzes.
Die Pfeile deuten den theoretischen Äquivalenzpunkt an.

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schnell. Es ist jedoch nicht nötig, anfangs auf eine konstante Einstellung des Galvanometers zu warten. Der Strom vor dem Äquivalenzpunkt ist die Folge der Elektrodenreaktion

$$Hg_2Cl_2 + 2\ e \rightleftarrows 2\ Hg + 2\ Cl^-$$

Nach dem Äquivalenzpunkt wird der Strom durch die Anwesenheit von Quecksilber(I)-Ionen erzeugt.

Der Endpunkt der Titrierung ist also viel schärfer feststellbar als mit Hilfe eines Adsorption-Indikators[13].

Wir haben daher den Titer der Quecksilber(I)-lösung unter Verwendung von Natriumchlorid als Ursubstanz ermittelt, auch schon deswegen, weil eventuell in der Titrierlösung vorhandenes Quecksilber(II)-salz durch das Quecksilber der Elektroden nahezu völlig in Quecksilber(I)-salz umgewandelt wird, sodass der Titer daher etwas höher sein kann als der mit den üblichen Methoden ermittelte.

Umgekehrt kann man auch ein bekanntes Volumen Quecksilber(I)-lösung in das Titriergefäss vorlegen und dann mit einer eingewogenen Natriumchloridlösung titrieren. Das Galvanometer stellt sich dann vom Anfang an schnell ein (Fig. 1b).

Die anzulegende Spannung beträgt in diesem und verwandten Fällen $\frac{1}{2}$ — 1 mV. Sie ist beim Äquivalenzpunkt bedeutend höher. Zu grosse Spannungen erzeugen im Galvanometer Schwankungen.

Beim Vergleich der Normal-Potentiale Ag/Ag^+ und Hg/Hg_2^{+2} zeigt sich, dass sie sich bloss um 1 mV unterscheiden[14]. Dies brachte uns auf den Gedanken unter Beibehalten der Quecksilberelektroden die Quecksilber(I)-lösung durch Silbernitrat zu ersetzen. Die so modifizierte Durchführung verlief auch sehr befriedigend. (Fig. 1c)

Bromidbestimmung

Diese verläuft völlig identisch mit der vorhergehenden Titrierung (Fig. 1d und 1e).

Jodidbestimmung

Wenn Quecksilber(I)-nitrat mit Jodid titriert wird, bildet sich anfangs ein grüngelbes Präzipitat, das während des weiteren Verlaufes der Titration allmählich in orange-gelb übergeht. Das Diagramm zeigt gerade vor dem Endpunkt einen ganz kleinen Knick. Es dauert lange, bevor das Galvanometer sich konstant einstellt (Fig. 1f).

In der Annahme, dass es sich vielleicht um Adsorptionserscheinungen handelt, wurden dem Grundelektrolyt noch zusätzlich 10 g $Ba(NO_3)_2$ bezw. $Th(NO_3)_4$ zugesetzt. Es trat keine Verbesserung ein.

Die Titration von Silbernitrat mit Jodiden und die umgekehrte zeigen diese Erscheinung nicht. Die Titration von Jodiden mit Quecksilber(I)-salzen wurde im Hinblick auf die Dismutation im Anfangstadium nicht durchgeführt.

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Rhodanidbestimmung

Auch hier wurde die Titration von Rhodaniden mit Quecksilber(I)-salzen wegen der Möglichkeit von Dismutation nicht durchgeführt. Doch färbt im umgekehrten Falle das Präzipitat sich anfänglich etwas grau, aber knapp vor dem Äquivalenzpunkt wird der Niederschlag vollkommen weiss. Die Ursache dieser Erscheinung, die bereits wiederholt erwähnt wurde[15,16], ist noch nicht geklärt (Fig. 2b und 2c).

Cyanidbestimmung

Diese Bestimmung kann in zweifacher Art durchgeführt werden;

a) in schwach mit HNO_3 angesäuerter $NaNO_3$-Lösung, mit einer Quecksilber(I)-lösung;

b) in alkalischem Medium mit einer Quecksilber(II)-lösung;

a) die Cyanidlösung befindet sich in einer Bürette. Zusatz ergibt direkt eine Abscheidung von Quecksilber. Die Reaktiongleichung lautet

$$Hg_2^{+2} + HCN = Hg + Hg(CN)_2 + 2\ H^+$$

b) die Grundlösung enthielt in diesem Fall per 100 ml : 5 ml $2N$ KOH, 10 ml $5M$ $NaNO_3$ und 5 Gramm KBr. In der Bürette befindet sich die eingestellte Merkurilösung. Die Reaktionsgleichung ist hier

$$2\ CN^- + Hg^{+2} = Hg(CN)_2$$

Das Kaliumbromid verhindert, dass gegen Ende der Titration stellenweise Quecksilber(II)-oxyd ausgeschieden wird, das dann nur sehr langsam mit dem noch nicht gebundenen Cyanid reagiert. Der Endpunkt nach Methode b) ist etwas weniger scharf feststellbar als bei Methode a) (Fig. 2e).

Man machte noch Versuche mit einigen anderen Titrationen in einer Lösung von $NaNO_3$, die schwach mit Essigsäure angesäuert war, sowie von Oxalat, Azid und Cyanoferrat(II), die nichtlösliche Quecksilber(I)-verbindungen bilden. Die Löslichkeit war jedoch zu gross, um den Äquivalenzpunkt noch gut bestimmen zu können. Einen sehr scharfen Umschlag gab die Titration von Quecksilber(I) mit Thiosulfat, wobei sich sofort ein schwarzer Niederschlag bildete (Fig. 2f).

Wahrscheinlich infolge des Auftretens von Nebenreaktionen besteht in diesem Fall kein einfaches Verhältnis zwischen dem Quecksilber(I) und dem Thiosulfat beim Umschlagpunkt, nämlich

$$Hg_2^{+2} : S_2O_3^{-2} = 1.3 : 1$$

ZUSAMMENFASSUNG

Durch Anlegen einer Spannung von einigen Millivolt zwischen zwei Quecksilberelektroden und Messung des Stromes während des Titrierens sind die Äquivalenzpunkte einer Reihe von Reaktionen, die mit löslichen Quecksilber(II)-, Quecksilber(I)- oder Silbersalzen zustande kommen, genau feststellbar.

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SUMMARY

The "dead-stop" end-point methode gives good results by application of mercury electrodes in some titrations with silver or mercury(I) or (II) solutions.

RÉSUMÉ

En appliquant une tension de quelques millivolts entre deux électrodes de mercure et en observant le courant en fonction du réactif, on peut déterminer avec une grande précision le point équivalent de quelques réactions, utilisant des solutions d'argent et de mercure (I) et (II).

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HIGH FREQUENCY TITRATIONS INVOLVING CHELATION WITH ETHYLENEDIAMINETETRAACETIC ACID

III. DETERMINATION OF URANYL ION

by

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Ethylenediaminetetraacetic acid forms exceptionally stable chelate complexes with many mono, di, and tri-valent metal ions. High frequency (oscillometric) studies of these chelation reactions have been made[1], and titrimetric methods for the quantitative estimation of various divalent metals, based on oscillometric detection of end-points obtained with ethylenediaminetetraacetic acid as the titrant, have been reported[2]. The present study is an extension of the latter work and is significant because it provides a new method for the titrimetric determination of uranyl ion.

High frequency oscillators can be utilized for following the progress of titrations made with ethylenediaminetetraacetic acid or its salts, regardless of the type of reactions involved. In the reactions studied previously, metal ions or their complexes were reacted directly with the reagent. In the present study the oxy cation, UO_2^{+2}, is titrated and the experimental results give clear indication of the occurrence of a stoichiometric reaction. That this reaction takes place is of special interest because previous investigators have failed to indicate the formation of stable uranyl-ethylenediaminetetraacetate chelates, although a salt having the composition, $UO_2H_2(C_{10}H_{12}N_2O_8) \cdot H_2O$, was reported by BRINTZINGER AND HESSE[3]. This compound, however, was isolated by dissolving solid ethylenediaminetetraacetic acid in aqueous uranyl acetate solution and the authors pointed out that the salt differed from the usual complexes because it lacked stability. They found that the salt readily decomposed to yield hydroxide precipitation, which is in contrast with the behavior of complex chelates of such metals as copper or nickel which resist hydroxide precipitation and most other characteristic reactions. Because of its lack of stability in solution, the uranyl salt of ethylenediaminetetraacetic acid has many of the characteristics of normal salts. Its very instability has been put to advantage by PRIBIL AND VORLICEK[4] who precipitate uranium by addition of ammonium hydroxide from solutions masked with ethylenediaminetetraacetate to prevent precipitation of other heavy metals that might be present.

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Other attempts to produce complexes of uranyl ion and ethylenediaminetetraacetic acid have been unsuccessful[5] although CABELL has suggested[6] that a reaction, 2 $UO_2^{+2} + H_2Y^{-2} \rightarrow (UO_2)_2Y + 2\ H^+$, takes place. CABELL further points out that the salt formed must be very unstable as evidenced by the normal precipitation reaction shown upon addition of hydroxide. He was unable to show conclusive evidence of the 2 to 1 reacting ratio (UO_2^{+2} to H_2Y^{-2}) from his potentiometric titration data because the curves obtained were not well defined. Qualitative indication of reaction was presented by CABELL in the form of his observation that mixing di-potassium ethylenediaminetetraacetic acid with uranyl nitrate yielded a mixture having a pH of 3. A distinct drop in pH was even noted when uranyl ion was added to the free acid form of the addendum.

The present study was undertaken when it was observed that the high frequency oscillator gave certain indication of a reaction between ethylenediaminetetraacetate and uranyl ion. Titration curves which were obtained were so definitive that further studies were justified to show the nature of the reaction involved and to explore its practical significance.

EXPERIMENTAL

Reagents and chemicals

All chemicals used were of reagent grade. Uranyl nitrate solutions were standardized gravimetrically by precipitating the hydroxide, igniting, and weighing as U_3O_8. Di-, tri- and tetra-sodium salts of ethylenediaminetetraacetic acid were used as titrants. For preliminary studies, the titrants were standardized by high frequency titration against standard calcium and copper solutions. Standard tri-sodium ethylenediaminetetraacetate solutions used in studying the titrimetric determination of uranyl ion were standardized directly against pure uranyl nitrate.

Apparatus

The high frequency oscillator used was a Sargent Model V Oscillometer. The cell compensator (variable inductance unit) was not employed although its use does permit considerable control of instrument sensitivity. Its use would be warranted where unknown samples were to be titrated and variation in instrument loading would be anticipated. A Model G Beckman pH meter was used for measuring hydrogen ion concentrations.

Reaction studies of uranyl-ethylenediaminetetraacetic acid based on liberation of hydrogen ions

When solutions of uranyl nitrate are mixed with ethylenediaminetetraacetic acid solutions, the pH of the mixture is found to be lower than that of either of the original members. This drop in pH is an indication that chelation takes place with a consequent release of hydrogen ions from the addendum. The conclusion must be drawn that direct reaction occurs in solution. By measuring released hydrogen ions through high frequency titrations, it should be possible to establish reaction ratios[1]. The following studies along such lines were made.

One hundred ml portions of 1/3032*M* ethylenediaminetetraacetic acid were titrated with 1/91*M* sodium hydroxide in the presence of varying amounts of uranyl nitrate. The ratios of uranyl ion to addendum were distributed so as to encompass all possible reacting ratios, and the resulting titration curves were plotted as shown in Fig. 1.

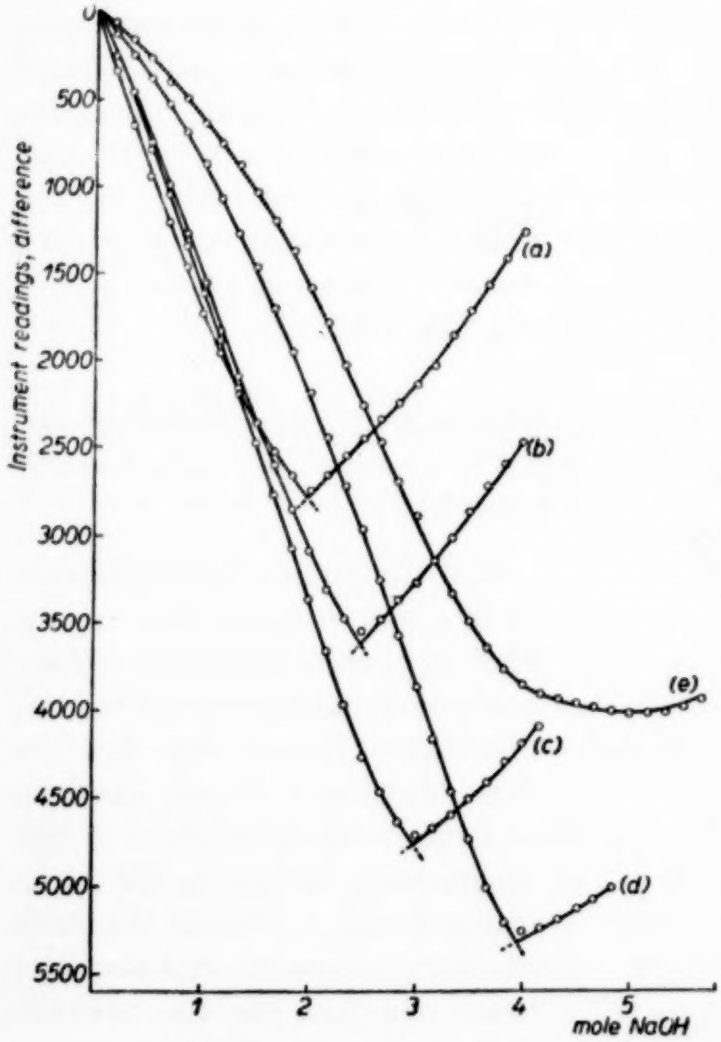

Fig. 1. Titrations with uranyl nitrate and ethylenediaminetetraacetic acid and with sodium hydroxide.

(a) Addendum only
(b) 1 : 2 (UO_2^{+2} addendum)
(c) 1 : 1 (do.)
(d) 2 : 1 (do.)
(e) 3 : 1 (do.)

As shown by the plotted data, the addendum by itself gives the anticipated inflection point at 2 mol equivalents of added sodium hydroxide. With the addition of uranyl nitrate, the reversal point shifts progressively with increasing ratios of uranyl ion to addendum. At a ratio of 2 to 1 (UO_2^{+2} to addendum) the release of hydrogen ions reaches a maximum which corresponds to 4 mol equivalents of base.

All titration curves drop smoothly to sharp inflection points until after the ratio reaches 2 to 1, giving curves similar to those obtained with such strong complexing metals as copper, zinc, cobalt, and nickel. For ratios greater than 2 to 1, the titration curve drops sharply but fails to give a distinct inflection at 4 mol equivalents of base.

Instead, the curve continues to drop slightly until finally a smooth reversal is obtained. For 3 to 1 ratios the reversal is reached at approximately 5 to 5.5 mols of base. This reversal probably represents the combined volumes of base required to neutralize liberated hydrogen ions and react with excess uranyl ions. Within the stoichiometric ratio of 2 to 1, the amount of titratable hydrogen ions is quantitatively related to the amount of uranium present.

Reacting ratios by direct titration

The reaction ratio of uranyl ion to ethylenediaminetetraacetic acid of 2 to 1, as determined by the hydrogen ion liberation technique, should be capable of substantiation by direct oscillometric titration. Experiments to confirm this supposition were conducted by titrating 100 ml portions of 1/2000*M* (or 1/3000*M*) uranyl nitrate using 1/200*M* disodium or 1/300*M* tetra-sodium ethylenediaminetetraacetate. As shown in Fig. 2, titrations with the di-sodium salt yield curves with distinct breaks, while the tetra-sodium salt gives curves showing poorly defined reversals. In both cases, the inflection obtained in the titration curve indicates a reaction ratio of 2 to 1. Similar titrations with trisodium ethylenediaminetetraacetate give even clearer indication of the 2 to 1 reaction ratio.

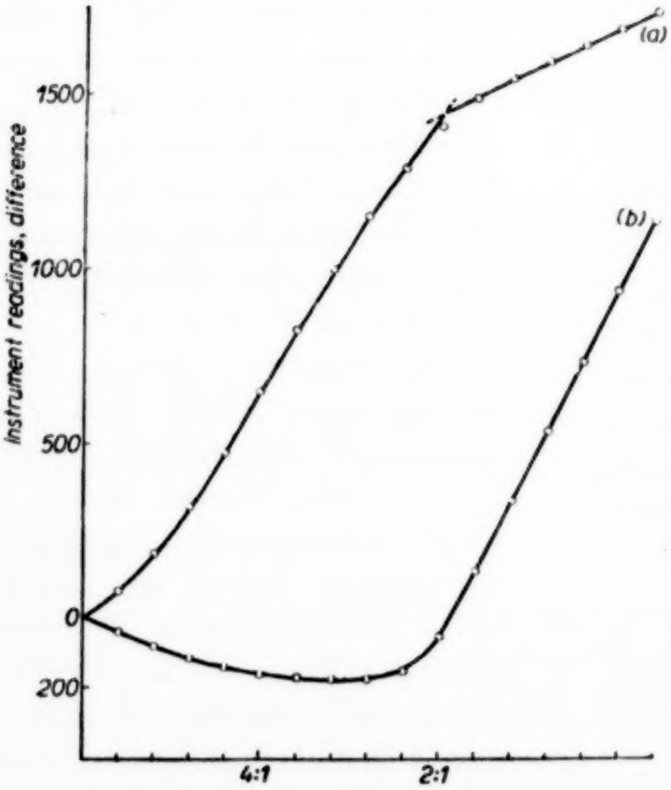

Fig. 2. Titrations of uranyl nitrate with di- and tetra-sodium salts of ethylenediaminetetraacetic acid.
(a) Titration of 1/3000*M* uranyl nitrate with 1/300*M* disodium ethylenediaminetetraacetic acid
(b) Titration of 1/2000*M* uranyl nitrate with 1/200*M* tetrasodium ethylenediaminetetraacetic acid

Quantitative determination of uranium by means of compleximetric titrations

The titrimetric determination of uranium through the use of high frequency detection of end-points is indicated by the studies mentioned above. The indirect determination based on the stoichiometric liberation of hydrogen can be accomplished as shown in Fig. 1. Within the ratio of 2 to 1, the quantity of standard base necessary for the neutralization of released hydrogen ions is proportional to the amount of uranyl ion present.

Another approach for the quantitative determination of uranium is to employ a direct titration

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using tri-sodium ethylenediaminetetraacetate as the titrant. As shown in Fig. 2, both the di-or tetra-sodium salt give inflections at the titrimetric end-point. The tri-sodium salt, however, has been found to give particularly sharp end-points and is therefore the recommended titrant. Various titration curves of tri-sodium ethylenediaminetetraacetate are shown in Fig. 3.

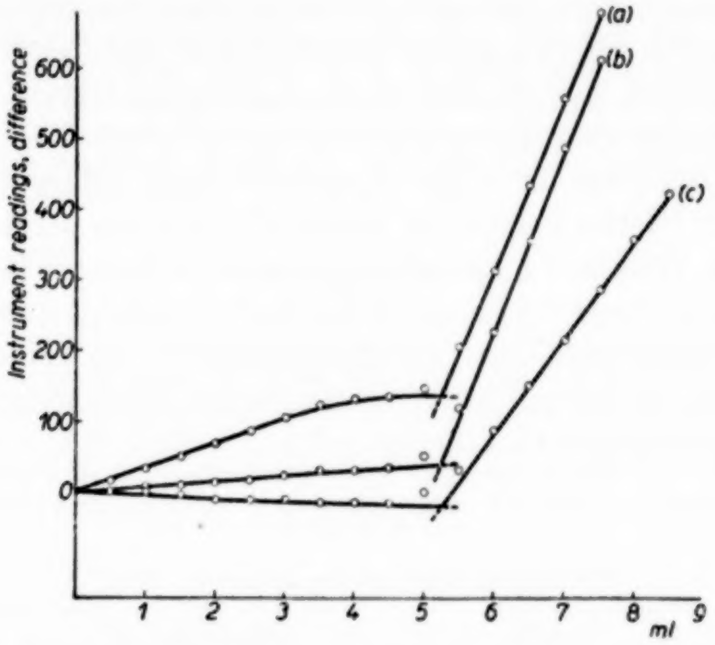

Fig. 3. Titrations of uranyl nitrate with trisodium ethylenediaminetetraacetic acid.
(a) Titration of 1/502*M* uranyl nitrate with 1/52.5*M* trisodium ethylenediaminetetraacetic acid
(b) Titration of 1/1000*M* uranyl nitrate with 1/105*M* trisodium ethylenediaminetetraacetic acid
(c) Titration of 1/3000*M* uranyl nitrate with 1/315*M* trisodium ethylenediaminetetraacetic acid

The recommended procedure for quantitative determinations employing the Sargent Oscillometer is to place 100 ml of the sample in the titration cell of the instrument. The sample should have a concentration range of 1/500 to 1/3000*M* and should have a pH in the range of 3.5 to 4.0. The sample is then titrated with tri-sodium ethylenediaminetetraacetate which has previously been standardized against pure uranyl salts. The titration end-point is indicated as a sharp break in the titration curve. Some typical results are shown in Table I.

Because the reagent is non-specific it must be used only under selected conditions. All heavy metals react with the reagent and so tend to interfere. Barium, strontium, silver, thallium (I) and the alkali metals are without interfering action except for loading effects on the oscillator. The possibility of interferences arising because of the presence of various anions was investigated. Acetate and oxalate interfere seriously and sulfate tends to reduce the sharpness of the end-point. Chloride, iodide, bromide, iodate, bromate, chlorate, and nitrate do not interfere except for loading effects which are common to all electrolytes (Table II).

DISCUSSION

Ethylenediaminetetraacetic acid reacts with uranyl ion to form a relatively unstable chelate. The oscillometric titration of uranyl ion with ethylenediaminetetraacetic acid and its salts shows that the reacting ratios of metal to addendum is 2 : 1 in this case, while heavy metals normally react to form 1 : 1 chelates with this complexing agent. Because of the unusual reacting ratio and because of the instability of the reaction product, it is felt that the uranyl-ethylenediaminetetraacetate compound is a chelate of the pseudo salt type.

Although the ethylenediaminetetraacetate salt of uranium has limited stability, as evidenced by precipitation of the hydroxide upon addition of strong bases, it is apparent that for the narrow pH range of 3.5 to 4.0 a relatively stable salt must be produced. Within the specified pH range, a distinct break in the uranyl ion titration curve is shown by means of the high frequency oscillator and quantitative results are obtainable when standard titrant is employed. Direct titration of uranyl ion using tri-sodium ethylenediaminetetraacetate is suggested for the quantitative determination of uranium.

TABLE I

DETERMINATION OF URANYL ION

UO_2^{+2}, mg taken	UO_2^{+2}, mg found	Molarity of titrant, M	Error %
27.04	26.86	1/105	0.67
27.04	26.82	1/105	0.81
9.000	9.083	1/315	0.92
9.000	8.964	1/315	0.40

TABLE II

DETERMINATION OF URANYL ION IN THE PRESENCE OF DIVERSE IONS

UO_2^{+2}, mg taken	Electrolyte added, mg	UO_2^{+2}, mg found	Error %
9.000	8.70, K_2SO_4	9.034	0.38
9.000	16.40, K_2SO_4	masked	—
9.000	16.6, KI	9.021	0.12
9.000	7.45, KCl	9.896	0.01
9.000	13.00, $Ba(NO_3)_2$	8.825	1.94
9.000	16.99, $AgNO_3$	8.983	0.19

References p. 291.

ACKNOWLEDGEMENTS

The authors wish to thank the E. H. Sargent company for financial support. The Berswerth Chemical Company kindly supplied ethylenediaminetetraacetic acid and its salts.

SUMMARY

It has been shown that for the pH range of 3.5 to 4.0, ethylenediaminetetraacetic acid reacts with uranyl ion to form a stable salt. The reacting ratio was found to be 2 : 1 (metal to addendum) which is in contrast to the usual reacting ratio of 1 : 1 obtained with ethylenediaminetetraacetic acid and other heavy metals. The chelate obtained with uranyl ion is probably a pseudo salt.

A high frequency titration employing tri-sodium ethylenediaminetetraacetate is suggested for the determination of uranyl ion.

RÉSUMÉ

Il est démontré que pour des pH compris entre 3.5 et 4.0, l'acide éthylènediaminotétraacétique réagit avec l'ion uranyle pour donner un sel stable. Dans ce cas le rapport métal/réactif est 2/1 (différence avec d'autres métaux lourds pour lesquels ce rapport est 1/1). Le chélate obtenu avec l'ion uranyle est probablement un pseudosel. Une titration à haute fréquence utilisant le dérivé trisodique de l'acide éthylènediaminotétraacétique est proposée pour le dosage de l'ion uranyle.

ZUSAMMENFASSUNG

Es wird gezeigt, dass die Ethylendiaminotetraessigsäure mit dem Ion Uranyl ein beständiges Salz bildet bei pH-Werten zwischen 3.5 und 4. Für diesen Fall ist die Proportion Metall/Reaktiv 2/1 (im Unterschied zu andern Schwermetallen, für die diese Proportion 1/1 beträgt). Das mit dem Uranyl-ion erhaltene Chelat ist wahrscheinlich ein Pseudosalz. Eine Hochfrequenztitration, welche das Trinatriumsalz der Ethylendiaminotetraessigsäure anwendet, wird vorgeschlagen für die Bestimmung des Ions Uranyl.

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MERCURY-MERCUROUS ACETATE INDICATOR ELECTRODE FOR POTENTIOMETRIC TITRATIONS IN ANHYDROUS ACETIC ACID

by

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In titrations in non-aqueous solvents, which in recent years have received a great impulse, the point of equivalence is determined either by means of suitable indicators, or by means of potentiometric procedures. The system of electrodes generally used is that represented by the glass-calomel electrodes. As reference electrode, the calomel electrode has been always considered appropriate; while, as indicator electrode, several types have been tried before the use of the glass electrode became general.

HALL, CONANT AND WERNER[1,2,3] conducted the first titrations in anhydrous acetic acid by means of a chloranil indicator electrode; this type of electrode was adopted in place of the quinhydrone electrode used in aqueous medium.

Later on, TOMIČEK[4] pointed out that the quinhydrone electrode is suitable also for titrations in acetic medium. However, the glass electrode is to be preferred to the two above-mentioned types, provided that a potentiometer, with a sufficiently sensible amplification, is available.

TOMIČEK AND HEYROVSKÝ[6] have used electrodes of antimony and tellurium which, however, are inconvenient because equilibrium is reached after a long period of time, and the tellurium electrode also gives too small potential changes.

For titrations in acetic medium MARKUNAS AND RIDDICK[7], SEAMAN AND ALLEN[8], PIFER AND WOLLISH[10,11], and others, always used the system of glass-calomel electrodes.

On the contrary, FRITZ[5] and KEEN AND FRITZ[9] adopted the system glass-Ag/AgCl.

The electrical communication of the two electrodes is achieved by means of salt bridges, closed at both ends with sintered glass stoppers, filled with a supersaturated solution of LiCl in acetic acid[1,2,3,8], or a saturated solution of LiCl in 96% ethyl alcohol[4].

The salt bridge may be eliminated by using a fibre-type calomel electrode directly dipped into the solution being examined; however, according to PIFER

AND WOLLISH[10], in some cases such a use is to be avoided because the calomel electrode may be easily contaminated with consequent change of its own potential.

The present work describes a new type of indicator electrode, which we used for neutralization titrations in anhydrous acetic acid. Besides having the advantages of being inexpensive and easy to prepare, it can be used also in connection with a common potentiometer without amplification.

The electrode consists of metallic mercury covered with mercurous acetate. It is an electrode of the second order, whose potential depends on the concentration of acetic ions in the solution in which it is dipped. In fact, the electrode of the second order consists of a metal covered with a conducting coating of a sparingly soluble salt of this metal; if the electrode is dipped in solutions containing the same anion of the above salt, it acquires a potential which depends on the concentration of the anion, on the value of the salt's solubility product and on the normal potential of the metal.

With the $Hg/Hg_2(CH_3COO)_2$ electrode it is possible to follow a neutralization titration in anhydrous acetic acid; in fact, according to BRÖNSTED[12], the following equilibrium subsists in the acetic solution:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

or more exactly: $$2\,CH_3COOH \rightleftharpoons CH_3COO^- + CH_3COOH_2^+$$

Consequently, an acetic solution will react, acid, neutral or basic, depending on whether the concentration of the hydrogen ions is more, the same or less than that of the acetic ions.

In the course of a neutralization titration in anhydrous acetic acid, the concentration of hydrogen and acetic ions undergoes reciprocal variations as a result of successive additions of titrating solution, reaching a maximum of variation at the equivalence point. To the variations of concentration correspond variations of the indicator electrode's potential. The changes of hydrogen ion concentration are followed by means of the glass electrode, and those of acetic ion concentration by the $Hg/Hg_2(CH_3COO)_2$ electrode. Therefore, these two electrodes are practically equivalent, even if they differ in constitution.

We have found by experiments that the $Hg/Hg_2(CH_3COO)_2$ electrode can replace advantageously the glass electrode for titrations in anhydrous acetic acid.

The comparison could be carried out indirectly, following the suggestions of SEAMAN AND ALLEN[8], concerning the color variations of the crystal violet indicator which must be taken into consideration with regards to the equivalence point of different titrations.

The electrodes of the second order have been used mainly for the realization of reference standard half-cells (the various calomels, the mercury cathode of a

Weston cell, the Ag/AgCl electrode for solutions containing chlorides[13]) and in some cases as indicator electrodes for potentiometric titrations. With Ag and Hg electrodes, covered with the corresponding halides or sulphides, HILTNER[14] carried out determinations of halogens, of Zn, Ni and cyanides, basing such a use on the principle that, if the concentration of an anion in a solution changes by adding other substances, the resulting variation of potential may be used for the determination of the anion or of the cations reacting with it.

Our work consisted in determining — by the method of SEAMAN AND ALLEN — the normality of an anhydrous acetic solution of $HClO_4$, approximately 0.1 N, using crystal violet as indicator and acid potassium phthalate as a standard substance; later the normality of the solution was redetermined by potentiometric procedures through our system of electrodes consisting of $Hg/Hg_2(CH_3COO)_2$ — saturated (in water) KCl agar bridge — saturated calomel, using acid potassium phthalate and sodium carbonate as standard substances, and potentiometers with and without amplification.

Preparation of the $Hg/Hg_2(CH_3COO)_2$ electrode

A gold wire, approximately 7 cm long and 1 mm thick, with a little plate, 2-3 mm in diameter, at one end, is covered with a glass jacket which leaves uncovered only the lower plate surface and 1 cm of wire at the upper end of the electrode, to allow for electrical communications.

The surface of the gold plate — covered with Hg, and this latter with mercurous acetate — is immersed in the solution and constitutes the active part of the electrode.

The technique of preparation is as follows:

Cleaning. The electrode is subject to anodical electrolysis in an alkaline solution of KCN (with a platinum cathode at 4 volts) for no less than 5 minutes. This operation is extremely important because, if not performed with the utmost care, it might compromise the whole preparation.

Mercury coating. The electrode, washed with water, is subject for a few minutes to cathodic electrolysis (with a platinum anode at 4 volts) in an acid solution of mercury nitrate (obtained by dissolving mercury in nitric acid) until a small hemispherical mass of mercury is obtained; during the electrolysis it is necessary to tap gently in order to release the gas bubbles resulting from the co-deposition of hydrogen on the mercury mass.

Acetate coating. The electrode, washed with acetic acid, is subject to anodic electrolysis (with a platinum cathode at 4 volts) in a solution of acetic acid 1N for one or two minutes. During this operation the mass of mercury became covered with a white salt coating which, when the operation is well performed, appears homogeneous and smooth. On the contrary, if the electrode is not carefully prepared, the coating of acetate may present wrinkles or black or grey colored stains. In these cases the electrode can also be used, but the potential values are different.

The electrode is next washed with anhydrous acetic acid and is then ready for use.

In a well prepared electrode the mercury must cover completely the gold and the mercury acetate must cover the mercury.

An electrode may be used for more than one titration (up to five); however, it is preferable to prepare it afresh for each titration.

The detachment, even partial, of the acetate coating (which may be caused by the contact with a rough surface or by a too strong blow) makes the electrode unfit for use. The handling of this electrode requires the same care as a glass electrode.

If, for any reason, the coating of acetate detaches itself during a titration, the potential value drops immediately and the reading will fluctuate noticeably.

Reduction of the acetate-coating thickness may occur perhaps as a result of the solution's dissolving action, or of the eroding action due to the agitation, or as a result of both.

The potential values of the $Hg/Hg_2(CH_3COO)_2$ electrode dipped in an acetic solution, depend on the acetate-coating thickness, which is a function of the time of electrolysis and varies within 40 mV; the more the thickness, the higher the value. Yet, the potential decreases with a rapidity proportional to the magnitude of the initial value (the higher the initial value, the quicker the potential decreases) and stabilizes itself at approximately +0.49 V (against saturated calomel). For this reason, if the coating turns out too dense, we advise waiting, before starting any titration, till the potential becomes stationary. Usually it is necessary to wait for one minute and only rarely for five minutes.

As soon as a mercury electrode without the acetate coating is dipped into a solution, it acquires for a short period of time almost the same potential of an electrode coated with acetate; then its potential decreases rapidly and readings become difficult because the pointer of the galvanometer oscillates continuously.

System of electrodes

The system of electrodes consists of saturated calomel-saturated (in water) KCl agar bridge-$Hg/Hg_2(CH_3COO)_2$.

On the early stages of our work we used fibre type calomel electrodes, dipped directly into the examined solution; the results obtained were too discordant and too low for the normality of the solution of $HClO_4$. We soon found out that, during the titration, the calomel electrode discharged in the acetic solution small quantities of saturated KCl solution. Further tests showed that both water and

KCl have an influence on the potential: in fact, the former hydrates the solvent and the latter reacts with the acetate coating of the electrode.

Therefore, it was necessary to use a salt bridge. Excellent results were obtained with the saturated (in water) KCl agar bridge, although this kind of bridge seemed to be rather unsuitable, according to the literature. One end of salt bridge, as well as a calomel reference electrode, was immersed in the saturated aqueous KCl solution and the opposite end in the acetic solution to be titrated. When the bridge is not in use, this opposite end must be immersed in anhydrous acetic acid.

As soon as the bridge has been prepared, one end of the same must be immersed in anhydrous acetic acid, for at least one day, before using it. This bridge may be used for an indefinite number of titrations and it seems to be preferable to any type of bridge.

Procedure

The titrations were conducted in open beakers without taking any care to avoid the contact with the surrounding air; we have never observed, during titrations, any influence due to absorption of moisture.

The volume of the solution to be titrated amounts to approximately 40 ml; the withdrawal of the titrating solution is effected by means of a 10 ml, 1/20 burette.

The $Hg/Hg_2(CH_3COO)_2$ electrode, the agar bridge and a glass stirrer were dipped into the solution, the stirrer was actionated by a small water motor which is to be preferred to electric or magnetic motors and to hand stirring.

The two electrodes, of which the calomel is the negative one, are connected with the potentiometer by means of simple electric wires.

The potentiometers used were a Cambridge tube-potentiometer and a Pehavi H. and B. potentiometer without amplification.

After the addition of each increment of titrating solution the potentials stabilize themselves in approximately 1 minute.

All determinations were made at the temperature of 16-18° C.

The acetic solution of $HClO_4$, the anhydrous acetic acid and the 1% solution of crystal violet have been prepared in the usual manner. All substances and reactives used were c.p.

Results

The normality of the $HClO_4$ solution, approximately $0.1N$, was determined by means of acid potassium phthalate and crystal violet (five drops of the 1% solution for an initial volume of 40 ml).

The value obtained was the mean of a series of 11 measurements.

Biphthalate g	$HClO_4$ ml	N
0.0760	3.90	0.09542
0.1220	6.30	0.09482
0.2527	12.95	0.09555
0.2165	11.10	0.09551
0.0698	3.57	0.09574
0.0846	4.33	0.09567
0.0811	4.15	0.09569
0.1211	6.23	0.09518
0.0324	1.66	0.09557
0.0727	3.75	0.09493
0.0395	2.05	0.09481

Average: 0.09535
Standard deviation: ±0.00030

The value obtained potentiometrically for the normality of the $HClO_4$ solution with our system of electrodes and with biphthalate was the mean of a series of 13 measurements.

Biphthalate g	$HClO_4$ ml	N
0.1025	5.27	0.09524
0.1207	6.18	0.09564
0.1224	6.27	0.09550
0.1326	6.83	0.09501
0.1427	7.35	0.09503
0.1232	6.35	0.09500
0.1418	7.27	0.09543
0.0984	5.05	0.09532
0.1463	7.52	0.09522
0.1874	9.64	0.09516
0.1247	6.45	0.09473
0.1030	5.27	0.09578
0.1360	7.03	0.09474

Average: 0.09521
Standard deviation: ±0.00025

By the potentiometric method with sodium carbonate, the normality of the solution has resulted from a series of 9 determinations.

Biphthalate g	$HClO_4$ ml	N
0.0926	18.51	0.09435
0.0909	18.22	0.09412
0.1203	23.87	0.09508
0.1575	31.35	0.09479
0.0913	18.11	0.09510
0.0707	14.07	0.09479
0.0857	17.03	0.09496
0.0612	12.25	0.09429
0.0752	15.05	0.09427

Average: 0.09464
Standard deviation: ±0.00038

These values are somewhat lower than the former; lower values were also obtained by SEAMAN AND ALLEN.

The above determinations were performed with a portable 1939 Cambridge potentiometer with amplification.

In order to demonstrate the possibility of using potentiometers without amplification, the normality of the $HClO_4$ solution was determined, with biphthalate, and with a Pehavi H. and B. potentiometer.

The value obtained was the mean of a series of 15 measurements.

Biphthalate g	$HClO_4$ ml	*N*
0.1113	5.87	0.09278
0.1110	5.66	0.09608
0.1045	5.43	0.09424
0.1048	5.38	0.09546
0.1023	5.34	0.09381
0.0741	3.87	0.09331
0.0852	4.35	0.09586
0.0842	4.34	0.09489
0.1041	5.35	0.09530
0.1165	5.88	0.09700
0.1463	7.52	0.09522
0.1247	6.45	0.09471
0.1030	5.27	0.09578
0.1524	7.87	0.09482
0.1360	7.02	0.09482

Average: 0.09494
Standard deviation: ±0.00082

From the above data we can see that the mean value agrees fairly well with those supplied by the Cambridge potentiometer, but the standard deviation results higher. This is to be ascribed to the fact that the Pehavi H. and B. potentiometer is less precise than the Cambridge apparatus.

Titrations of any type of substance with our system of electrodes are under way or being planned, in order to determine the applicability in the field of potentiometric titrations in anhydrous acetic acid and the possibility of using this method as a substitute for the glass-calomel system.

SUMMARY

The authors describe a metallic mercury electrode covered with a mercurous acetate coating, its preparation, its use as an indicator electrode in anhydrous acetic acid neutralization titrations and its properties as compared with other electrodes used for the same purpose.

References p. 299.

RÉSUMÉ

Les auteurs décrivent une électrode recouverte d'une couche d'acétate mercureux, sa préparation, son emploi comme électrode indicatrice pour les titrations par neutralisation dans l'acide acétique anhydre, ses propriétés comparées à celles des autres électrodes employées pour les mêmes recherches.

ZUSAMMENFASSUNG

Die Autoren beschreiben eine Quecksilberelektrode, die mit einer Schicht Quecksilber(I)acetat überzogen ist, ihre Präparation, ihre Verwendung als Indikator-Elektrode für Neutralisations-Titrationen in wasserfreier Essigsäure; ihre Eigenschaften im Vergleich zu denen anderer Elektroden, welche für die gleichen Forschungen verwendet werden.

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BOOK REVIEWS

Successful Commercial Chemical Development, prepared by the Commercial Chemical Development Association with H. M. Corley as editor-in-chief, J. Wiley, New York, 1954, 374 pages, $ 7.75.

Although development in chemical industry is based in the first place on the work in the chemical and physical research laboratory, the eventual success of a new process or of a new product depends on the activity in several other departments. Organized commercial development started in the early forties. Every new product must pass through certain stages and a number of factors must be investigated to avoid unprofitable expenditures which may be considerable in case of an eventual failure. In our days discovery and development are no longer the result of accident, but of planned research. The development of the nylon and the synthetic rubber industries are striking examples of chemical research combined with intentional process development, integrated with product and market evaluation.

The present volume has been prepared by several committees of specialists and discusses the principles of every essential step in selecting new chemicals and developing them to the stage of economic importance.

Of the subjects treated we mention the evaluation of new product ideas and projects, in their several development stages, the trade names, labeling, shipping, toxicologing and safe handling.

The book is a most valuable contribution and covers a very important and interesting subject.

H. A. J. Pieters (Geleen)

Chromatography, British Medical Bulletin Vol. X, 3, 1954.

Dans ce numéro spécial du Bulletin, les auteurs ont essayé de mettre en évidence la très grande importance des méthodes chromatographiques pour la biochimie et (indirectement) pour la Médecine.

Dans ce but, ils ont réuni un choix d'articles, dus à des spécialistes connus, et couvrant les principaux groupes des matières présentant un grand intérêt biochimique ou médical.

Le premier article est consacré à l'exposé général des principes de la chromatographie qui sont à la base des différents types: chromatographie d'adsorption, de partition et par échange d'ions. L'analyse par élution graduelle, moins employée jusqu'ici, y est également décrite.

La technique de James et Martin pour la chromatographie de systèmes „gaz-liquide" et l'analyse de matières volatiles, y est décrite par les auteurs eux-mêmes dans le second article. Nous apprécions particulièrement la description de cette nouvelle méthode très importante et susceptible de nombreuses applications, mais peu connue jusqu'ici.

On pourrait regretter qu'on n'y ait pas ajouté un article sur la méthode dite „counter current distribution" et sur l'électrophorèse sur papier.

Le 3ème article décrit la technique de la chromatographie sur papier et attire l'attention sur quelques aspects spéciaux d'intérêt pratique pour les non initiés.

Dans les articles suivants, exception faite pour un exposé de Pollard sur la chromatographie inorganique, des spécialistes traitent chacun la séparation et l'analyse d'un groupe déterminé de matières organiques très importantes pour la biochimie.

Les biochimistes et tous ceux qui s'intéressent à l'étude de mélanges très complexes de matières difficilement accessibles par les méthodes chimiques ordinaires, y trouveront certainement des renseignements très utiles.

J. Eeckhout (Gand)

THE STANDARDIZATION OF AMMONIUM VANADATE SOLUTIONS WITH SODIUM OXALATE

by

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The reaction between quinquevalent vanadium and oxalic acid has been the subject of a number of investigations, the results of which have been contradictory. In 1892, ROSENHEIM AND FRIEDHEIM[1] suggested the use of oxalic acid for estimating the concentration of vanadate solutions. More recently, SYROKOMSKII AND KLIMENKO[2] have reported that no reaction occurred, this finding being borne out by the work of RAO *et al.*[3] On the other hand, TSUBAKI[4], RAO AND SANKEGOWDA[5], and MORETTE AND GAUDEFROY[6] have indicated that oxalic acid is completely oxidized by means of acidic vanadate solutions. BOBTELSKY AND GLASNER[7] have studied the rate of reduction of vanadic acid with oxalic acid; however, the reaction conditions imposed for their study were such as to be of little interest from the standpoint of practical analytical chemistry.

The present investigation was undertaken in an effort to resolve in some measure the conflicting statements appearing in the literature, and to determine whether sodium oxalate would be a suitable primary standard for vanadate solutions. To date, the principal methods for the standardization of vanadates have involved the use of Mohr's salt or potassium dichromate. It would thus be of value to have available a supplementary substance for this function; the widespread availability of sodium oxalate would render it very useful for this purpose.

Under the reaction conditions employed, it has been found that oxalic acid is rapidly and quantitatively oxidized by acid solutions of ammonium *m*-vanadate. The reaction may be represented by the following equation:

$$2VO_3^- + H_2C_2O_4 + 6H^+ \rightarrow 2VO^{+2} + 2CO_2 + 4H_2O$$

The oxidation is carried out in the presence of an excess of vanadate in a strong (>50%) sulfuric acid medium. Upon diluting and cooling, the excess oxidant is titrated with a ferrous ammonium sulfate solution, using *N*-phenylanthranilic acid as indicator. The volume ratio of ferrous ammonium sulfate to vanadate is determined at the same time. Neither the excess of vanadate nor the sulfuric acid concentration is critical. Attempts to carry out the titration directly were not successful.

REAGENTS

Ammonium m-vanadate, approximately 0.3 normal. About 33 g of C.P. ammonium *m*-vanadate were dissolved in 900 ml of distilled water and 100 ml of concentrated sulfuric acid (d. 1.84). The solution was filtered through a sintered-glass crucible. Standardization was normally carried out against a ferrous ammonium sulfate solution of accurately known normality.

Ferrous ammonium sulfate, approximately 0.12 normal. About 120 grams of ferrous ammonium sulfate hexahydrate were dissolved in 2250 ml of distilled water and 250 ml of concentrated sulfuric acid. The titer of this solution was determined daily by titration with primary standard potassium dichromate.

Ferrous ammonium sulfate hexahydrate. Mohr's salt having a purity factor of 99.91% was used throughout this investigation where accurately weighed amounts of this substance were required.

N-phenylanthranilic acid, 0.066 molar. 0.213 g of Eastman Kodak N-phenylanthranilic acid was dissolved in 30 ml of 5% aqueous sodium carbonate; this was then diluted to 150 ml with distilled water. Three to five drops of the resulting solution were employed for each titration.

Sodium oxalate. National Bureau of Standards # 40 Oxidimetric Standard sodium oxalate was used. Samples were either introduced with a calibrated volumetric pipet as 10 ml aliquots of prepared solutions or were weighed out directly; in the latter instance, they were dissolved in 10 ml of 10% sulfuric acid.

Potassium dichromate. Use was made of primary standard grade potassium dichromate in the form of a 0.1 normal solution.

PROCEDURE

A 10 ml aliquot of the vanadate reagent was transferred to a 250 ml Erlenmeyer flask containing the oxalate sample. Approximately 25 ml of concentrated sulfuric acid were then cautiously added. The flask was swirled to mix the contents; where a water-bath was not employed, the time required for the reaction was counted from this operation. Upon completion thereof the solution was diluted by the careful addition of 100 ml of distilled water; after thorough mixing by swirling, the flask was allowed to cool to room temperature, following which the excess vanadate was titrated with ferrous ammonium sulfate solution until the blue color of vanadyl sulfate was distinct. Then several drops of N-phenylanthranilic acid solution were added and the titration continued until the purple color of the indicator changed to bright green. While the indicator is stable toward a large excess of oxidant in the cold, it was found expedient to defer its addition until most of the excess vanadate was consumed, since little warning is given of the onset of color-change. Further, it was found advisable to proceed slowly toward the end of the titration in order to avoid over-running of the end-point. Where sodium oxalate was used for the determination of vanadate normality, it was necessary to obtain a volume ratio between the ferrous and the vanadate solutions. The procedure employed for this was the same as that described above, except that no oxalate was involved.

STOICHIOMETRY

Effect of heating period

Using the foregoing procedure, weighed samples of sodium oxalate were oxidized with ammonium *m*-vanadate at the temperature of a boiling water-bath for periods of 1-60 minutes. As shown in Table I, the reaction was complete in every instance. The heating requirements necessary for a quantitative reaction were then further examined; aliquot portions of an oxalate solution were employed in this case. Since the addition of sulfuric acid to the vanadate-oxalate mixture resulted in the evolution of a considerable amount of heat, the possibility of dispensing with the water-bath was investigated. Following addition of the sulfuric

TABLE I

OXIDATION OF SODIUM OXALATE AS A FUNCTION OF THE HEATING PERIOD

Quantity NH_4VO_3 taken, milliequivalents	Quantity $Na_2C_2O_4$ taken, millimols	Heating time, minutes	$\frac{\text{Eq. vanadate consumed}}{\text{Mol sodium oxalate}}$	
3.018	0.8626	60	2.010	Heated on water-bath, 100°C
3.018	0.8708	30	2.007	,, ,, ,, ,, ,,
3.018	0.9029	16	1.995	,, ,, ,, ,, ,,
3.018	1.057	5	2.006	,, ,, ,, ,, ,,
3.018	1.020	5	1.997	,, ,, ,, ,, ,,
3.018	1.020	4	1.995	,, ,, ,, ,, ,,
3.018	1.020	3	1.997	,, ,, ,, ,, ,,
3.018	1.020	2	2.000	,, ,, ,, ,, ,,
3.018	1.020	1	1.997	,, ,, ,, ,, ,,
3.018	1.020	0	1.991	Immediately diluted.
3.018	1.020	0	1.997	1 Minute elapsed before dil.
3.018	1.020	0	1.995	2 ,, ,, ,, ,,
3.018	1.020	0	1.997	3 ,, ,, ,, ,,
3.018	1.020	0	2.004	4 ,, ,, ,, ,,

acid, the samples were allowed to stand for varying periods of time prior to the addition of water. Again referring to Table I, it was found that allowing a few minutes to elapse between the addition of sulfuric acid and the dilution with water was sufficient to assure a complete oxidation of the oxalic acid. In subsequent work, the time for reaction varied from 3-10 minutes with no apparent effect upon the results.

Influence of sulfuric acid

In order to investigate the dependence of the reaction upon the acid concentration, samples of sodium oxalate were oxidized with ammonium *m*-vanadate in sulfuric acid media ranging from 50-60%. At least three minutes were allowed to elapse between the addition of the acid and dilution with water. It was found (Table II) that within this range, the sulfuric acid concentration is not critical with respect to the reaction; however, the indicator was observed to change color in a rather sluggish fashion during back-titration of samples representing the two lower acid concentrations.

TABLE II

OXIDATION OF SODIUM OXALATE AS A FUNCTION OF THE SULFURIC ACID CONCENTRATION

Quantity NH_4VO_3 taken, milliequivalents	Sulfuric acid		Quantity sodium oxalate	
	ml	% by vol	taken, millimols	found, millimols
3.018	18	50	1.020	1.020
3.018	20	52	1.020	1.018
3.018	22	55	1.020	1.018
3.018	24	57	1.020	1.020
3.018	26	59	1.020	1.020
3.018	28	60	1.020	1.018

Use of sodium oxalate as a primary standard for vanadate solutions

The suitability of sodium oxalate as a primary standard for vanadate solutions was investigated by concurrently standardizing a solution of the latter against (a) Mohr's salt of known purity, (b) primary standard potassium dichromate indirectly through the agency of a standardized ferrous ammonium sulfate solution, and (c) sodium oxalate of primary standard purity. Sodium oxalate was found to be a perfectly satisfactory material against which to determine the titer of vanadate solutions. The results of these determinations are summarized in Table III.

TABLE III

STANDARDIZATION OF A VANADATE SOLUTION

Against sodium oxalate			Against potassium dichromate*		Against Mohr's salt		
Quantity taken, grams	N	deviation	N	deviation	Quantity taken, grams	N	Deviation
0.1001	0.3185	0.0006	0.3174	0.0002	0.9946	0.3170	0.0005
.1148	.3188	0.0009	.3172	.0004	1.0399	.3173	.0002
.1277	.3181	.0002	.3171	.0005	1.0611	.3177	.0002
.1338	.3178	.0001	.3174	.0002	1.0626	.3176	.0001
.1354	.3186	.0007	.3179	.0003	1.1257	.3173	.0002
.1367	.3178	.0001	.3173	.0003	1.1280	.3174	.0001
.1428	.3182	.0003	.3176	.0000			
.1431	.3172	.0007	.3173	.0003			
.1433	.3187	.0008	.3183	.0007			
.1450	.3184	.0005	.3181	.0005			
.1470	.3172	.0007	.3178	.0002			
.1472	.3181	.0002	.3180	.0004			
.1476	.3176	.0003	.3175	.0001			
.1503	.3172	.0007	.3175	.0001			
.1513	.3170	.0009	.3175	.0001			
.1517	.3185	.0006	.3177	.0001			
.1613	.3186	.0007	.3177	.0001			
.1629	.3168	.0011	.3177	.0001			
.1634	.3176	.0003					
.1660	.3176	.0003					
.1739	.3183	.0004					
.1768	.3180	.0001					
.1796	.3176	.0003					
.1802	.3179	.0000					
.1803	.3179	.0000					
.1822	.3180	.0001					
.2016	.3180	.0001					
Averages	0.3179	0.0004	0.3176	0.0003		0.3175	0.0002

* Since the titer of the ferrous ammonium sulfate solution used for these titrations was obtained by reference to primary standard potassium dichromate, the normality of the vanadate solution is thus indirectly referred to this latter substance.

DISCUSSION

Inspection of the data contained in Table III shows that a satisfactory agreement exists among the several methods of standardization. In effect, these titrations were carried out against the three primary standard substances, sodium oxalate, potassium dichromate, and Mohr's salt. The average normality values fall within a range only slightly greater than one part per thousand. The standard deviation of 0.0005 in the case of the oxalate titrations is somewhat greater but still compares favorably with 0.0003 when a standardized ferrous ammonium sulfate solution was employed, and 0.0003 for the few standardizations carried out against weighed samples of Mohr's salt. It is worthy of note that samples of the reducing agents used as primary standards in this work were titrated with a solution of ceric sulfate according to customary procedures and were found to give concordant results. Likewise, the standard Mohr's salt was titrated with the dichromate solution; satisfactory checks were again obtained. Thus it was found that excellent internal consistency existed between the various standard substances; that they continued to show this in the case of the vanadate standardizations is indicative of the validity of the method in question.

It is of interest to note that no correlation exists between the weight of oxalate taken and the value for vanadate normality obtained.

Several attempts were made to titrate sodium oxalate directly with a solution of ammonium *m*-vanadate; none was successful. The reaction was found to proceed too slowly at room temperature to be of analytical importance, while at elevated temperatures, the indicator was rapidly attacked by any quinquevalent vanadium which was momentarily present. In one instance, an acidified sample of sodium oxalate was titrated at about 100°; addition of the first drop of vanadate reagent caused formation of the oxidized form of the indicator, the color of which persisted after further heating. In another experiment the titration was carried to within one milliliter of the theoretical end-point prior to the addition of indicator. Upon adding a drop of the latter, the oxidized form immediately appeared, which again was not discharged by further heating. Osmium tetroxide failed to exhibit any catalytic effect upon the reaction.

A potentiometric titration at 95° was carried out, making use of a Beckman Model G pH meter equipped with a platinum and a calomel electrode. Even at this temperature, the reaction proceeded quite slowly, as evidenced by the prolonged drift of the meter readings after each addition of reagent; this effect became more pronounced as the end-point was approached. The end-point break in the curve was found to be about 3.5% premature. While it is possible that some improvement over this figure might have been attained by suitable adjustment of experimental conditions, no attempt was made to do so in view of the very long period of time required to carry out the titration.

SUMMARY

The results of a study of the reaction between ammonium *m*-vanadate and sodium oxalate in strong sulfuric acid solution are given. It has been found that the latter is a suitable and convenient primary standard for solutions of quinquevalent vanadium.

RÉSUMÉ

Une étude a été effectuée sur la réaction métavanadate d'ammonium et oxalate de sodium, en solution sulfurique concentrée et les résultats sont donnés. L'oxalate de sodium peut être utilisé comme étalon pour titrer le vanadium (V).

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ZUSAMMENFASSUNG

Die Reaktion von Ammoniummetavanadat mit Natriumoxalat in konzentrierter Schwefelsäurelösung wurde untersucht und die Resultate werden gegeben. Das Natriumoxalat kann als Vergleich verwendet werden bei der Titration von Vanadium (V).

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COMPLEXOMETRIC TITRATION OF ALUMINIUM *

by

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Many attempts have been made to replace the troublesome and inaccurate gravimetric aluminium determination by a volumetric method.

Formerly, a solution of sodium fluoride was, as a rule, used as titrant[1,2], but since SCHWARZENBACH AND BIEDERMANN[3,4] showed that aluminium forms very stable complex compounds with ethylenediaminetetraacetic acid (EDTA, H_4Y) and other "complexones", the newer methods have usually been based upon the use of these reagents.

SCHWARZENBACH AND BIEDERMANN suggested a method in which the hydrogen ions liberated in the reaction between the disodium salt of EDTA and aluminium ions were titrated. However, the results were not satisfactory, and the method seems to be of little use. PŘIBIL[5] tried a potentiometric method, in which the excess of the complexing agent was back-titrated with an iron-III-chloride solution. MILNER AND WOODHEAD[6] also used this titrant in a visual method. As indicator they employed salicylic acid at a pH of 6.5. Another visual method has been proposed by TER HAAR AND BAZEN[7], who add an excess of EDTA and back-titrate with thorium nitrate, using alizarine sulphonate as indicator. The solution is buffered to a pH value of 4.3 and has to be boiled before titration. This method gives values 1 % too low, but since the error is constant the authors suggest the use of an empirical factor. FLASCHKA, TER HAAR AND BAZEN[8] have recently modified this method. In the titration of aluminium ions, in amounts less than 1 mg at a pH value of 4, good results were obtained, but for larger amounts of aluminium the errors were about 1 to 2 %. SAJÓ[9] has employed zinc sulphate for the back-titration of the excess EDTA, using eriochromecyanine as indicator at a pH between 5 and 7. A similar method was recently described by PŘIBIL, ČIHALIK, DOLEŽAL, SIMON AND ZÝKA[10], who used eriochromeblack T as indicator.

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* Part of this paper was presented by A. RINGBOM at the Symposium on Analytical Chemistry, held by the Midland Society for Analytical Chemistry at Birmingham in August 1954.

RINGBOM, WÄNNINEN AND SIITONEN[11] devised still another method. They add the complexing agent in excess to the solution and titrate the excess with a copper sulphate solution at pH = 5, using murexide as indicator. Theoretical considerations on the basis of the equilibrium constants showed that in this case nitrilotriacetic acid ("Complexone I") as titrant would be more advantageous than EDTA. The visual detection of the end-point was not successful, but rather precise results were obtained by the use of a photoelectric method (*cf.* RINGBOM AND WÄNNINEN[12]).

In order to make possible a visual detection of the exact end-point, we tried to back-titrate the complexing agent — in this case EDTA — with a zinc sulphate solution, using dithizone as indicator. This indicator dissolved in carbon tetrachloride has recently been used by BOVALINI AND CASINI[13], who titrated lead and cadmium with EDTA. The method suggested by these authors is, however, not very convenient, as the shaking of the two-phase mixture until equilibrium is attained takes considerable time. RINGBOM, NYMAN AND WÄNNINEN[14] have found that in the titration of EDTA with zinc sulphate solution in an alcohol-water or in an acetone-water mixture, dithizone gives an extremely sharp colour change from greenish-violet to red at a pH of about 4.5.

The compound formed is $ZnDz_2$, where dithizone is denoted by HDz. The authors mentioned determined the complexity constant K_{ZnDz_2},

$$\frac{[ZnDz_2]}{[Zn^{+2}]\,[Dz^-]^2} = K_{ZnDz_2} \tag{1}$$

using a value of $K_{HDz} = 10^{-4.6}$ for the acidic dissociation constant, and obtained a value of $K_{ZnDz_2} = 10^{10.8}$ in 40 % alcoholic solution. The ionic strength of the solution was about 0.01.

The value given for K_{ZnDz_2} is a concentration constant, calculated on the assumption that the pH value of the buffered alcohol-water solution is the same as in the absence of alcohol. Although this is not quite correct, measurements at lower alcohol concentrations gave about the same value. The determination of activities in alcohol-water mixtures offers many difficulties. Hence the calculation of equilibrium constants on the basis of concentrations rather than from activities is often appropriate in analytical chemistry, especially since it is in concentrations that the analyst is essentially interested.

The colour change may be assumed to occur at the point where half of the indicator is bound to the complex as $ZnDz_2$. In other words, $[Dz^-] = \frac{1}{2} C_{ind}$ and $[ZnDz_2] = \frac{1}{4} C_{ind}$, where C_{ind} is the total concentration of the indicator. This means that at pH values larger than about 6 the colour change occurs at

$$[Zn^{+2}] = \frac{1}{K_{ZnDz_2}\, C_{ind}} \tag{2}$$

For titrations in acid solutions it is advantageous to calculate an apparent constant $K'_{\mathrm{ZnDz_2}}$:

$$\frac{[\mathrm{ZnDz_2}]}{[\mathrm{Zn^{+2}}]\,([\mathrm{Dz^-}]+[\mathrm{HDz}])^2} = \frac{K_{\mathrm{ZnDz_2}}}{\left(1+\dfrac{[\mathrm{H^+}]}{K_{\mathrm{HDz}}}\right)^2} = K'_{\mathrm{ZnDz_2}} \qquad (3)$$

The colour change then occurs at

$$[\mathrm{Zn^{+2}}] = \frac{1}{K'_{\mathrm{ZnDz_2}}\,C_{\mathrm{ind}}} \qquad (4)$$

The point of colour change at various pH values and at various indicator concentrations can easily be obtained from Fig. 1.

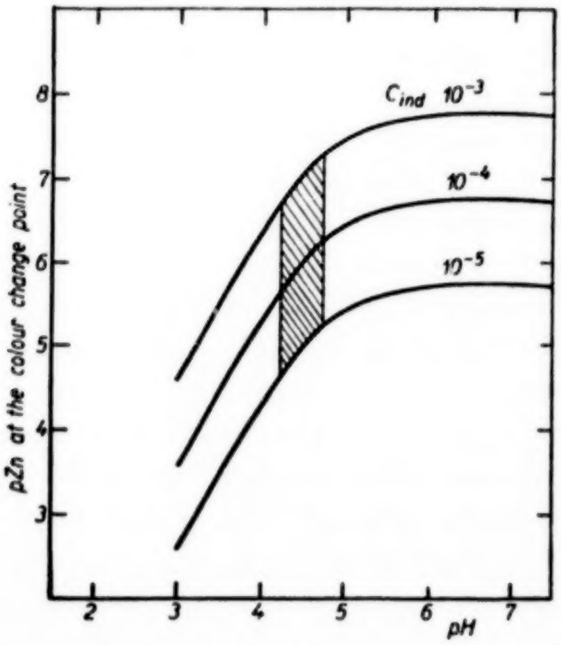

Fig. 1. pZn at the colour change point as a function of the acidity and of the indicator concentration.

It is obvious that dithizone is more sensitive than many of the metal indicators hitherto used at least in acid solution. pZn at the colour change point is about 6, and it can be increased to a still higher value by increase in the indicator concentration. However, if the indicator concentration is high, consideration must be given to the amount of metal bound to the indicator; if necessary, a correction $[\mathrm{Zn^{+2}}] \approx \frac{1}{4}\,C_{\mathrm{ind}}$ should be applied.

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For the theoretical treatment of the method suggested above a knowledge of the complexity constants of AlY and ZnY is necessary. Recently SCHWARZENBACH, GUT AND ANDEREGG[15] determined these constants, obtaining for K_{AlY} the value $10^{16.1}$; for K_{ZnY} they give a value of $10^{16.5}$ in approximate agreement with the former value of $10^{16.2}$.

As the colour of dithizone depends on the zinc ion concentration, it is important to know pZn at the equivalence point. At this point the following equation must be satisfied:

$$\sum_{i=0}^{4} [H_iY] = [Zn^{+2}] + [Al^{+3}] \tag{5}$$

On the other hand, the following expressions are also valid:

$$[Al^{+3}] = \frac{K_{ZnY}}{K_{AlY}} \cdot \frac{[AlY^{-}]}{[ZnY^{-2}]} [Zn^{+2}] \tag{6}$$

$$[Y^{-4}] = \beta \sum_{i=0}^{4} [H_iY] \tag{7}$$

β is the fraction of the reagent not bound as a complex that appears as Y^{-4} ions; *i.e.*

$$\beta = \frac{[Y^{-4}]}{[H_4Y] + [H_3Y^{-}] + [H_2Y^{-2}] + [HY^{-3}] + [Y^{-4}]} \tag{8}$$

The values of β can easily be determined from a graph in which log β is plotted as a function of pH.[12]

From equations 5,6 and 7 it is readily seen that

$$[Zn^{+2}] = \sqrt{\frac{[ZnY^{-2}]}{\beta K_{ZnY}\left(1 + \frac{K_{ZnY}}{K_{AlY}} \cdot \frac{[AlY^{-}]}{[ZnY^{-2}]}\right)}} \tag{9}$$

This expression is graphically presented in Fig. 2 for pH = 4 and pH = 4.5.

Fig. 2 shows that pZn at the equivalence point is between 6 and 7 when the aluminium concentration ranges from 10^{-2} to $10^{-3}M$ and when about a 10 % excess of the complexing agent is used ($[ZnY^{-2}] \approx 10^{-3}$ to 10^{-4}). This pZn value is not far from the middle of the colour change interval of dithizone (Fig. 1). Accordingly a sharp colour change would be expected. However, if too large an excess of EDTA is used, the equivalence point will occur at lower pZn values;

the colour change will then not be sufficiently sharp and the consumption of zinc solution may very well be too small, *i.e.* the aluminium values may be too large. On the other hand, according to Fig. 2, the results will change in the opposite direction if the excess of EDTA is very small.

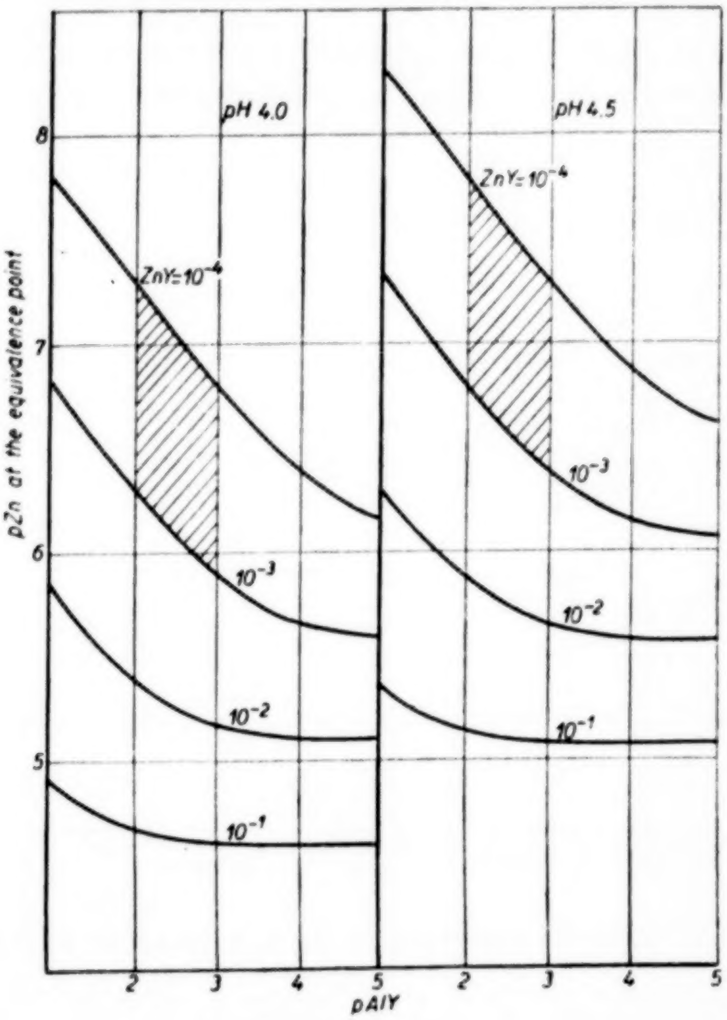

Fig. 2. pZn at the equivalence point at various concentrations of AlY^- and ZnY^{-2} at pH = 4.0 (left) and pH = 4.5 (right).

The influence of pH on the results may be seen by comparison of the curves of Fig. 2. Theoretically, a low acidity should be advantageous if equations 5 to 8 are valid. However, at pH above about 4.5 the formation of aluminium hydroxo complexes affects the equilibrium and poor results are obtained, as will be shown later in this paper.

The curves of Fig. 2 make it possible to calculate exactly the theoretical errors for titrations to defined pZn values. The calculations are based on the following equations, in which the quantities on the right side are known:

$$[Y^{-4}] = \frac{[ZnY^{-2}]}{[Zn^{+2}]\ K_{ZnY}} \qquad (10)$$

$$[\mathrm{Al}^{+3}] = \frac{[\mathrm{AlY}^{-}]}{[\mathrm{Y}^{-4}]\ K_{\mathrm{AlY}}} \tag{11}$$

$$\sum_{i=0}^{4} [\mathrm{H_i\,Y}=]\ \frac{[\mathrm{Y}^{-4}]}{\beta} \tag{12}$$

$$\text{Titration error, } \% = \frac{\sum\limits_{i=0}^{4} [\mathrm{HiY}] - [\mathrm{Al}^{+3}] - [\mathrm{Zn}^{+2}]}{[\mathrm{AlY}^{-}]} \times 100 \tag{13}$$

The results of a series of calculations are presented graphically in Fig. 3, where the titration error is plotted as a function of the excess of EDTA (= $[\mathrm{ZnY}^{-2}]$) at various concentrations of aluminium.

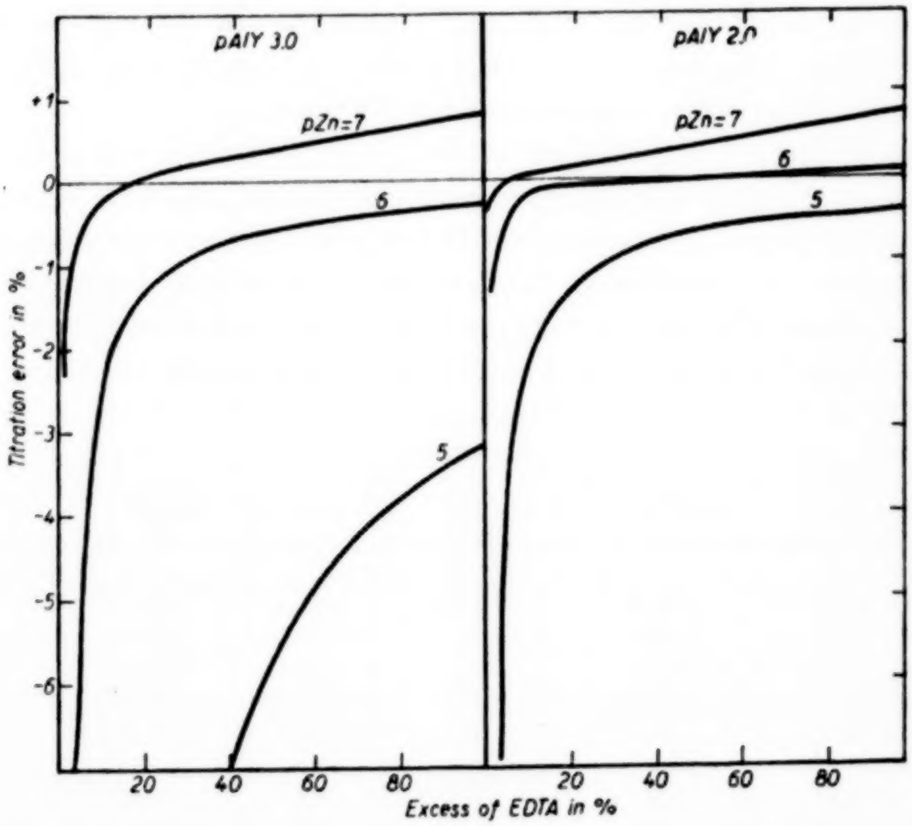

Fig. 3. Theoretical titration error as a function of the excess of EDTA and of pZn at the equivalence point at various concentrations of AlY^{-}. pH = 4.5.

The results given in Figs. 2 and 3 lay no claims to any high degree of exactness or of general validity, since the values of the equilibrium constants change considerably with the ionic strength. This effect will probably be particularly strong

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for K_{AlY} because of the high charges of the Al^{+3} and Y^{-4} ions. Complex formation with buffer substances possibly present (*e.g.* acetates) may also affect the equilibrium.

Nevertheless the calculations illustrate rather clearly the influence of various factors on the accuracy of the method. Moreover they illustrate a general procedure for the determination of the optimum experimental conditions in indirect complexometric titrations, and explain why in such determinations the results of various authors, obtained under various conditions, often do not agree very well.

The theoretical considerations given above led to the following procedure:

Procedure: To the sample solution containing 0.2-0.5 millimoles of aluminium a known volume of the Na_2H_2Y solution, corresponding to 0.3-0.7 millimoles, is added. The solution is buffered to pH 4.5 by the addition of 10 ml of an acetic acid-ammonium acetate buffer solution (1 mole acetic acid + 1 mole ammonium acetate liter). Alcohol is added to a concentration of 40-50 % by volume, and 2 ml of the 10^{-3} *M* indicator solution pro 100 ml (0.25 g dithizone/l alcohol) is pipetted into the mixture; the indicator solution should not be more than a few days old. The solution is now titrated with a 0.05 *M* zinc sulphate solution until the colour changes from greenish-violet to red.

The results of some titrations are given in Table I. The pH of the solution at the end-point was 4.2 to 4.6, *i.e.* somewhat smaller than the pH of the buffer solution, since hydrogen ions are liberated in the reaction between Na_2H_2Y and metal ions. It may be mentioned that, even if the sample solution is very acid, no acid-base indicator is needed for the regulation of the acidity, since dithizone itself serves as a pH indicator, changing colour from greenish to yellow at pH ≈ 4.6.

TABLE I

No.	EDTA mmoles	$ZnSO_4$ mmoles	Al taken mmoles	Al found mmoles	Error %	Remarks
1	0.4935	0.2941	0.1996	0.1994	—0.1	
2	0.4960	0.2482	0.2482	0.2478	—0.16	
3	0.4935	0.2442	0.2495	0.2493	—0.08	
4	0.7564	0.2632	0.4965	0.4932	—0.66	
5	0.7564	0.2572	0.4990	0.4992	+0.04	
6	1.4875	0.4894	0.9980	0.9981	+0.01	
7	1.2440	0.2382	0.9980	1.0058	+0.8	
8	0.5929	0.3967	0.1990	0.1962	—1.4	24 % alcohol
9	0.5929	0.3957	0.1990	0.1972	—0.9	32 % alcohol

The colour change was very sharp and the results are satisfactory. The alcohol content may be smaller than 40-50 %, but in that case the colour change is not quite so sharp. In experiments 8 and 9 (24 and 32% alcohol) the results were a little too low.

An unexpected source of error should be mentioned. At pH = 4.6 the results obtained were much too low if the buffer solution was added before the complexing agent. At lower pH the errors were smaller, and when the solution was buffered with potassium biphthalate (pH = 3.9; No. 12) good results were obtained even if the buffer solution was added first. The errors always disappeared when the solution was boiled before the back-titration. Table II illustrates these phenomena.

TABLE II

No.	pH	EDTA mmoles	$ZnSO_4$ mmoles	Al taken mmoles	Al found mmoles	Error %
10	2.95	0.4960	0.3063	0.1986	0.1897	−4.5
11	3.5	0.4960	0.3113	0.1986	0.1847	−7.0
12	3.9	0.4960	0.2983	0.1986	0.1977	−0.45 (a)
13	4.35	0.4960	0.3263	0.1986	0.1697	−14.5
14	4.4	1.4875	0.6660	0.9980	0.8215	−17.7
15	4.6	0.4960	0.3313	0.1986	0.1647	−17.1
16	4.6	0.3231	0.1615	0.1996	0.1616	−19.0
17	4.6	0.2982	0.1396	0.1996	0.1586	−20.0
18	4.6	0.4960	0.2983	0.2482	0.1977	−20.0
19	4.6	0.4960	0.2487	0.2482	0.2473	−0.36 (b)

(a) 10 ml of 0.05*M* potassium biphthalate as buffer solution.
(b) The solution was boiled before back-titration.

The low results obtained at pH = 3.5 or below (No. 10 and 11) are probably caused by the incompleteness of the reaction between EDTA and the metal ions, owing to the decrease of β with decreasing pH values.

It seems likely that the errors at higher pH are caused by the formation of aluminium hydroxo complexes, which react with EDTA more slowly than the aluminium ions. The fact that good results were obtained at pH = 3.9 but very low results at pH = 4.35 shows that there is a very sharp upper limit of pH for satisfactory titration.

The hydrolysis of aluminium ions has recently been treated by BROSSET[16]. He showed that on the acid side of the isoelectric point the following reactions take place:

$$Al^{+3} + Al^{+3} + 3\,H_2O = Al_2(OH)_3{}^{+3} + 3\,H^+ \quad k_1' = 10^{-10.3}$$

$$Al_2(OH)_3{}^{+3} + Al^{+3} + 3\,H_2O = Al_3(OH)_6{}^{+3} + 3\,H^+$$

$$Al_{n-1}(OH)^{+3}_{3(n-2)} + Al^{+3} + 3\,H_2O = Al_n(OH)^{+3}_{3(n-1)} + 3\,H^+ \quad k_1 = 10^{-9.2}$$

According to this scheme the formation of polynuclear hydroxo complexes is regulated by only two constants: k_1', determining the formation of the binuclear complex, and k_1, determining the formation of all the other complexes. The degree of complex formation at various pH values is illustrated by the curves in Fig. 4, where the complex formation number $\bar{n}$, *i.e.* the average number of OH^- groups bound per aluminium atom, is plotted as a function of pH.

Quite in accordance with our results, the curves show that the formation of hydroxo complexes starts rather suddenly within a very narrow pH interval.

It is possible to calculate a limiting value of pH at which the formation of hydroxo complexes can be neglected. This is done, considering only the binuclear $Al_2(OH)_3^{+3}$ complexes, which predominate in more acid solution. The relationship between the concentration of binuclear complexes and pH is given by

$$\frac{[Al_2(OH)_3^{+3}]\,[H^+]^3}{[Al^{+3}]^2} = k_1' = 10^{-10.3} \tag{14}$$

If, for instance, 99 % of the aluminium are in the form of Al^{+3} ions, we have

$$\frac{0.005\,[H^+]^3}{[Al^{+3}]} \approx 10^{-10.3} \tag{15}$$

or, considering that $[Al^{+3}]$ approximately equals $[Al]_{tot}$

$$[H^+]^3 \approx 10^{-8}\,[Al]_{tot} \tag{16}$$

In Fig. 5 is shown the straight line of pAl_{tot} plotted as a function of pH. These pH values are calculated from constants determined at 40° C and represent limits of more or less approximate character. Our experiments were performed

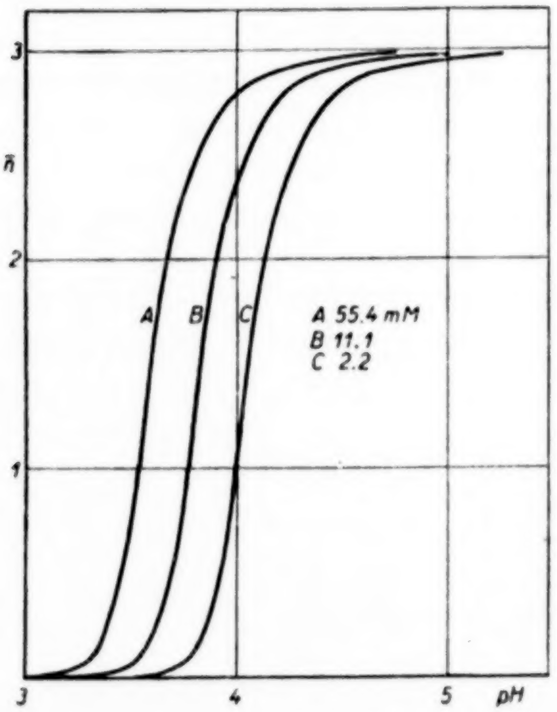

Fig. 4. Relationship between average complex formation number $\bar{n}$ and pH at various concentrations of aluminium, according to BROSSET.

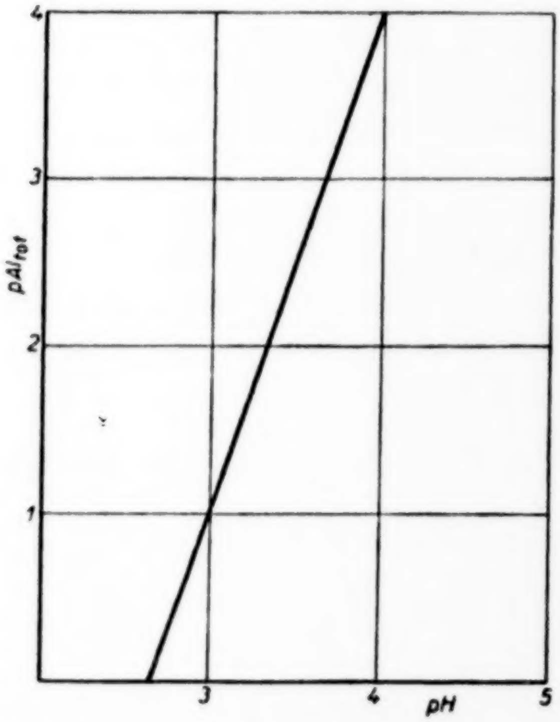

Fig. 5. Limiting value of pH at which the formation of aluminium hydroxo complexes can be neglected.

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at room temperature and in alcohol-water solutions. However, the experimentally obtained pH limits are in fairly good agreement with the pH values taken from the curve.

In case the buffer solution is added before the complexing agent the complexometric determination of aluminium is thus highly dependent on the acidity, and large errors will result at pH 4-5 unless the solution is boiled before the back-titration with zinc sulphate. EDTA, which reacts rapidly with the Al^{+3} ions in an acid solution, evidently reacts slowly with the polynuclear hydroxo complexes. This effect is particularly noticeable at high aluminium concentrations. However, it can be avoided simply by adding the complexing agent before the buffer solution at a pH of about 3.

The method described is affected by the presence of metals which react with EDTA at a pH < 4.5. If Fe-III-salts are present, the sum of Al + Fe will be determined.

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SUMMARY

A procedure is given for the complexometric titration of aluminium. A known volume of a standard solution of EDTA is added to the sample solution, and the excess is back-titrated with a zinc sulphate solution, dithizone being used as indicator. The titration is performed at pH = 4.0 — 4.5, and 40—50% alcohol is added as solvent for the indicator.

The theoretical basis of the method is developed, and the theoretical titration error with various amounts of aluminium and zinc is calculated.

The results of some titrations are given.

RÉSUMÉ

On propose pour le dosage de l'aluminium une méthode complexométrique. Une quantité connue d'EDTA est ajoutée à la solution à analyser, et l'excès est titré par une solution de sulfate de zinc, en se servant de dithizone comme indicateur. Le pH de la solution est 4.0—4.5; de l'alcool éthylique (40—50%) est ajouté pour dissoudre l'indicateur. Les bases théoriques de la méthode sont données et le calcul d'erreur est effectué pour différentes concentrations. Ce mémoire est accompagné des résultats de quelques titrations.

ZUSAMMENFASSUNG

Es wurde eine Methode für die komplexometrische Titration von Aluminium beschrieben. Die Versuchslösung wurde mit einem bekannten Volumen einer EDTA-Lösung versetzt, und der Überschuss wurde unter Verwendung von Dithizon als Indikator mit einer Zinksulfatlösung zurücktitriert. Die Titration geschah bei pH = 4.0—4.5 in Anwesenheit von 40 bis 50% Alkohol als Lösungsmittel für den Indikator.

Die Grundlagen der Methode wurden durch theoretische Überlegungen klargestellt, und der Titrierfehler wurde für verschiedene Konzentrationen von Aluminium und Zink berechnet.

Es wurde über das Resultat einiger Titrationen berichtet.

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THE OXIDATION OF THALLIUM(I) BY SELENIOUS ACID

by

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Of the various quantitative methods for the determination of thallium, those based on its precipitation as chromate[1] and iodide[2] are perhaps the most extensively used. A variety of precipitants has been reported recently and an interesting new field in the gravimetric estimation of thallium has also been opened by UMEMURA[3] and by PELTIER AND DUVAL[4] by determining the thermal stability of its compounds with the aid of the thermobalance. In all these processes the thallous salt is precipitated as such, or precipitation is effected after it is completely oxidized to Tl(III) by a suitable oxidant[5,6]. The oxidation from Tl(I) to Tl(III) forms incidentally the basis of many titrimetric and potentiometric studies[7,8]. It is known that selenious acid is reduced in presence of HCl by a number of powerful reducing agents. Preliminary experiments in these laboratories showed that the addition of thallous salt solution to H_2SeO_3, acidified with excess of HCl, produced the characteristic red precipitate of selenium. A detailed study of this interesting redox reaction was therefore undertaken with a view to evolving a new procedure for the quantitative determination of thallium. These observations have now been recorded in this communication.

EXPERIMENTAL

Thallous acetate solutions of various concentrations were prepared by dissolving appropriate quantities of Merck's reagent grade sample in water. The thallium content of each solution was determined by the classical iodate method[8]. An aliquot portion of the Tl(I) solution was taken in a round bottomed flask fitted with a ground glass seal condenser. A measured excess of an aqueous solution of selenious acid was now introduced in the flask followed by concentrated HCl and the overall acid concentration was maintained at or above $4N$. A red colloidal precipitate of selenium appeared almost immediately. The condenser was fitted in and the system was refluxed for about 20-30 minutes. The red precipitate turned brownish black and coagulated gradually during refluxing. The contents were cooled to room temperature, the condenser detached and the precipitated selenium was filtered through a weighed porous porcelain or Gooch crucible with an asbestos pad. The precipitate was washed thoroughly with cold water, then with a small quantity of absolute alcohol and ether. It was sucked dry, heated in an air oven at 90° C for about 20 minutes, cooled and weighed. From the weight of selenium thus obtained, the quantity of thallium was calculated according to the equation:

$$H_2SeO_3 \rightarrow H_2O + Se + O_2$$
$$2(CH_3COO)Tl + 6HCl + H_2SeO_3 \rightarrow 2TlCl_3 + CH_3(COOH)_2 + 3H_2O + Se \quad (I)$$
$$\text{or } 2Tl = 1Se$$

A typical set of results is given in Table I.

TABLE I

Overall acidity 4-5N HCl Normality of H_2SeO_3 0.1214N
Duration of reflux 30 min

Expt. No.	Vol. of Tl soln taken ml	H_2SeO_3 added ml	Wt of Se g	Wt of Tl g		Diff.
				Found H_2SeO_3 method	Calculated KIO_3 method	
1	10.0	5.0	0.0038	0.01968	0.01980	—0.00012
2	10.0	10.0	0.0048	0.02485	0.02465	+0.00023
3	10.0	10.0	0.0062	0.03210	0.03248	—0.00038
4	10.0	20.0	0.0084	0.04350	0.04356	—0.00006
5	20.0	25.0	0.0126	0.06525	0.06498	+0.00027
6	30.0	30.0	0.0188	0.09736	0.09714	+0.00022
7	40.0	40.0	0.0250	0.1290	0.1297	—0.0007

The close agreement between the calculated and observed values show that the accuracy of the results is satisfactory and that the above procedure is applicable to the determination of as small a quantity as 20 mg of thallium. Results of a series of experiments showed that even with a prolonged standing the oxidation of thallium is incomplete if the reaction is allowed to proceed at room temperature. Furthermore, the overall acidity of the medium is an important determinant of the reaction. With the hydrochloric acid concentration less than 1N only thallous chloride is precipitated and the red colloidal selenium is imperceptible. The reaction is slow even when the acidity is about 3N and at ordinary temperature the precipitated Se is still mixed up with that of thallous chloride. On increasing the concentration of HCl to 4N or above, the white thallous chloride disappears gradually on swirling and the dense red precipitate of Se coagulates. For a rapid and quantitative oxidation of Tl(I) to Tl(III) it is, however, desirable to reflux the system for at least 20-30 minutes.

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The significant role of HCl in this redox process is emphasized by the observation that thallous salts are not oxidized by H_2SeO_3 in the presence of even large concentrations of sulphuric, acetic or perchloric acid.

A useful and conclusive check for the accuracy of the results was afforded by the following experimental procedure. After the complete oxidation of Tl(I) to Tl(III) by a measured excess of H_2SeO_3, and the subsequent separation by filtration of the precipitated selenium, the filtrate was made up to an appropriate volume. An aliquot quantity of this solution was made alkaline by an excess of NaOH. The thallic hydroxide thus obtained was filtered, washed free of Cl′ and H_2SeO_3 and the filtrate was collected. The precipitate was dissolved in a minimum quantity of dilute HCl and after adding KI the liberated iodine was titrated potentiometrically with sodium thiosulphate[10]. The filtrate collected after separating $Tl(OH)_3$ was acidified with hydrochloric acid and its selenium content was determined iodometrically by thiosulphate or sodium arsenite[11] and/or by complete reduction to metallic selenium by any suitable reductant to find out the unreacted H_2SeO_3. This, together with the result calculated from the weight of selenium obtained initially, should obviously correspond to the quantity of selenious acid mixed with the thallous solution. Direct iodometric titration of the original H_2SeO_3 solution served as a conclusive proof for the validity of this anticipation.

According to equation (I) $2Tl = 1Se$, the small conversion factor does not permit an accurate determination of the quantity of Tl less than that given in Table I because of the lack of precision in weighing the precipitated selenium with a macro balance. It is therefore not claimed at the present stage that the above procedure is applicable to the estimation of micro or semi-micro quantities of thallium.

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SUMMARY

A new and simple method for the quantitative determination of thallium based on the oxidation of Tl(I) to Tl(III) by selenious acid has been described. The precipitated selenium is weighed directly. Furthermore, the thallic hydroxide obtained by the addition of excess alkali to the filtrate is dissolved in HCl and determined iodometrically. The excess selenious acid in the filtrate is also estimated iodometrically or by gravimetric method after reduction to metallic selenium. Under the specified operative conditions the results are reproducible and accurate within the limits of experimental error.

RÉSUMÉ

Une méthode nouvelle et simple est décrite pour le dosage du thallium par oxydation de Tl(I) en Tl(III) au moyen de l'acide sélénieux. Le sélénium précipité est pesé directement. D'autre part, l'hydroxyde de thallium(III), obtenu par

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addition d'un hydroxyde alcalin au filtrat, est dissous dans HCl et dosé iodométriquement. L'excès d'acide sélénieux du filtrat est également dosé par iodométrie ou par gravimétrie après réduction en sélénium élémentaire. Dans des conditions déterminées les résultats sont reproductibles et précis dans les limites d'erreur expérimentale.

ZUSAMMENFASSUNG

Es wird eine neue und einfache Methode beschrieben für die Bestimmung von Thallium durch Oxydation von Tl(I) zu Tl(III) mit Hilfe von seleniger Säure. Das ausgefällte Selen wird direkt gewogen. Anderseits wird das Hydroxyd von Tl(III), welches man durch Zugabe von einem Alkalihydroxyd zum Filtrat erhält, gelöst in HCl und iodometrisch dosiert. Der Überschuss der selenigen Säure im Filtrat wird ebenfalls iodometrisch bestimmt oder aber gravimetrisch nach der Reduktion zu elementarem Selen. Bei festgelegten Bedingungen sind die Resultate reproduzierbar und genau, in den experimentell festgelegten Fehlergrenzen.

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ESTIMATION OF THORIUM BY ORGANIC REAGENTS: RECOVERY FROM WORN-OUT GAS MANTLES AND TUNGSTEN FILAMENTS BY 2 : 4-DICHLOROPHENOXYACETIC ACID

by

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Introduction of thorium and other rare-earths into incandescent gas mantles in 1886, brought an epoch-making success in that industry, which had a modest beginning only two years earlier. The mantle, when it is used as an incandescent material, consists essentially of thoria with 1% of ceria in solid solution. The beryllia and magnesia are present in smaller quantities which only serve to increase the strength of the skeleton fibre[1]. A pure thoria mantle provides comparatively little light, as it is of non-radiant nature. The function of ceria is to cause the mantle to emit visible rays, which are maximum in the blue region of the visible spectrum; an excess quantity of ceria however, increases the emission of invisible rays and lowers the temperature due to increased radiation. Thus, an increase in the ceria content of the mantle beyond 1% decreases the luminosity of the lamp[2]. It has been estimated that the world's annual consumption of incandescent mantles is about 30 millions and the total quantity of thoria used annually for that purpose approximates to 150,000 kilograms[3]. Thus a huge quantity of thorium is used up and lost when the mantles wear out after long use. Owing to the pressing need of thorium in this and other industries, like the manufacture of photoelectric cells, glow-tube electrodes and as a source of atomic energy, the question of the recovery of thorium from worn-out mantles has attracted the attention of various workers in the field. H. S. MINER of Welsbach Company[4] extracted out thorium from the mantle residues by dissolving them in conc. sulphuric acid and precipitating the earths as oxalates. Thorium can, however, be recovered by the usual inorganic methods.

Another possible source of thorium from industrial waste is the worn-out tungsten filaments of fused electric bulbs, though usually only a very minute quantity of thorium is present in them. The filaments are made from the tungsten powder obtained by the reduction of tungsten trioxide to which is added a little thorium nitrate in order to give about 0.7 to 1 % of thoria in the finished product[5]. The function of thorium oxide is to reduce the growth of tungsten grains which occur during glowing and thus to prolong the life and activity of the filaments. The reduction of the oxide to thorium takes place during the burning of the electric lamps[6]. Though the quantity of thorium in such filaments is very small, the commercial exploitation of this metal from the worn-out filament of the fused electric bulbs is not impossible or uneconomic, if suitable methods of extraction are applied. Thorium can be recovered by dissolving the filaments in nitro-hydrofluoric acid and precipitating it as hydroxide, but this method is not suitable since a quantity of tungsten is always retained by the thorium precipitate. In an attempt to drive out tungsten as WCl_6, by heating the filament powder in a current of chlorine, LAMAR (1912) found that a quantity of thorium was also volatilized as $ThCl_4$ along with tungsten, and the latter was found to be converted to oxy-chloride. BROPHY AND BRUNT[7] however removed the disadvantage of the above process, by preventing the volatilization of thorium along with tungsten, using a mixture of chlorine and oxygen as chlorinating agent. Oxygen reacted with thorium chloride, formed during chlorination and converted it to the oxide according to the reaction:

$$ThCl_4 + O_2 = ThO_2 + 2\ Cl_2$$

But their method is also not very satisfactory, as the oxides of metals like Al, Ti, *etc.* and silica, if present in the filament, will not be volatilized away during chlorination.

The present paper deals with a process for the estimation and recovery of thorium from worn-out gas mantles and tungsten filament residues, with the help of 2 : 4-dichlorophenoxyacetic acid, technically known as 2 : 4-D. This acid has been successfully utilized by the authors for the estimation of thorium[8]. 2 : 4-D can precipitate thorium at a low pH (2.8), even in the cold, and it settles within 5 minutes without requiring any electrolyte like ammonium chloride *etc.* for its coagulation, and the precipitate is not soluble during washing. It can be separated from a number of metal ions; the presence of calcium, barium, strontium, magnesium, zinc *etc.* and the rare earths do not interfere in the estimation of thorium.

The earths present in the mantle-residues were converted into the sulphates according to the method of MINER *(loc. cit.)*. From this solution of the sulphates, thorium was recovered as a salt of 2 : 4-D, at a suitable pH. Thorium is found in a very small amounts in the filaments, and its recovery presents a difficult problem, since large quantities of worn-out filaments are necessary for the purpose. As it is known that during burning of the filaments the thorium oxide present in them is reduced to metallic thorium[9], the filaments were treated with aqua-regia to convert thorium to its soluble salts, and tungsten was left behind as yellow tungstic acid. Thorium was then extracted with 2 : 4-D from the filtrate at a definite pH. The recovery of thorium is not practicable by this method, unless a huge quantity of filaments can be procured and the solution after the removal of tungsten contains at least 0.002 g of thorium oxide per 20 ml solution. For preliminary investigation, the sample solutions were tested for thorium by suitable reagents.

REAGENTS AND MATERIALS REQUIRED

2 : 4-Di-chlorophenoxyacetic acid was prepared according to the modified method of GHOSH[10] from 2 : 4-dichlorophenol and monochloracetic acid. It was purified by crystallization from benzene until the melting point rose to 138° C. Its purity was also established from its equivalent weight determination (0.1 g of the acid dissolved in 10 ml of alcohol was titrated against $0.1N$ NaOH solution).

Solution of worn-out gas mantles. A considerably quantity of different samples of worn-out incandescent mantles were collected from the market shops. Stock solutions of these mantles were prepared by the following method: A known weight of sample was treated with the requisite quantity of conc. sulphuric acid for about 4 hours. The pasty mass was allowed to cool and was taken up with ice-cold water. The earth content of this solution was determined by the oxalic acid method.

Dissolution of tungsten-filaments. A huge stock of different samples of tungsten filaments from fused electric bulbs was kindly supplied by the Electricity Division, Darjeeling and the municipality, and they were also obtained from this college and the hostel attached to it. The filaments were broken into smaller pieces and ground to a powdery mass in an agate mortar. The samples thus prepared, were accurately weighed and then heated separately with aqua regia, nearly to dryness. The tungsten present in them was converted into bright yellow insoluble tungstic acid during this treatment. The residue was digested with water containing a little cinchonine solution to avoid the formation of colloidal tungstic acid. Tungsten was then estimated in each of the residues from the samples, according to the standard method of analysis of tungsten in steel[11]. The filtrates were brought to a definite volume before determining their thorium content.

EXPERIMENTAL

Recovery of thorium from gas-mantle solution

A definite volume of the different stock solutions of various gas-mantles, was brought to a pH between 2.8 and 3 by adding a dilute solution of NaOH. 50 ml of a hot 1.5% solution of 2 : 4-D in water was stirred into it. A white flocculent precipitate appeared at once and collected at the bottom of the beaker when warmed a little. The precipitate settled completely within 5 minutes, after which it was filtered through a No. 42 Whatman filter paper and washed with a hot 0.2% solution of the reagent and then five or six times with hot water. The paper and the contents were dried, charred and ignited to 1000° C, using platinum crucibles. The ThO_2 obtained after ignition was then cooled and weighed. The total earth content of the sample was determined by the standard oxalate method. The ThO_2 obtained with 2 : 4-D was compared with that obtained with *m*-nitro benzoic acid, which is also considered as a standard reagent for thorium[12]. The results are given in Table I.

TABLE I

ESTIMATION OR RECOVERY OF THORIUM FROM THE GAS-MANTLE SOLUTIONS

Wt of gas-mantle residue	Wt of total earth present (oxalic acid method)	Wt of ThO_2 present (*m*-nitro benzoic acid method)	Wt of ThO_2 found by 2 : 4-D	% recovery of ThO_2 from mantles by: *m*-nitro benzoic acid	2 : 4-D	No. of Detns.
Sample no. I						
0.5458 g	0.4931 g	0.4868 g	0.4883 g	89.19	89.48	4
0.5756	0.5201	0.5162	0.5168	89.66	89.76	4
0.6301	0.5695	0.5610	0.5652	89.00	89.66	4
0.3023	0.2732	0.2691	0.2710	89.02	89.66	4
Sample no. II						
0.4112	0.3710	0.3678	0.3682	89.48	89.54	3
0.4201	0.3796	0.3749	0.3760	89.13	89.52	3
0.5033	0.4541	0.4516	0.4501	89.73	89.39	3
Sample no. III						
0.5121	0.4626	0.4578	0.4582	89.49	89.48	3
0.4702	0.4242	0.4203	0.4200	89.39	89.33	3
0.4313	0.3890	0.3858	0.3870	89.45	89.73	3

It appears from Table I that the recovery of thorium from the different samples of the mantles is almost the same, *viz.*, an average of 98.5%, and this agrees well with the corresponding values obtained by *m*-nitrobenzoic acid. The thorium oxide successfully recovered from the gas-mantle residues by this method can be reconverted to the nitrate, for its utilization in industry.

Recovery or determination of thorium from tungsten filaments

About 30 g of different samples of filament residues were dissolved in aqua regia and the % of tungsten in them determined by standard method varied from 98.5 to 99.02%. Hence, the % of thorium present in them might be between 1.5 to 0.98%, assuming however, that other metals were absent in the filaments, and that even if they were present in traces they would not interfere in the determination of thorium with 2 : 4-D. Aliquot quantities of tungsten-free filament solutions were neutralized to pH between 2.8 and 3, by adding dilute ammonia. The volume of the solution was reduced to 20 ml by evaporation, and then an excess of 2% solution of 2 : 4-D was added to it. A thin precipitate appeared, which on boiling became coarser. The precipitate after washing and drying as before was ignited to the oxide. The oxide in the crucible was absolutely white in colour, and gave positive results when tested for thorium with appropriate reagents. The estimation with *m*-nitrobenzoic acid was not done side by side in this case, as it was considered unnecessary. The results are tabulated in Table II.

TABLE II

DETERMINATION OF THORIUM IN TUNGSTEN FILAMENTS

Sample No.	ThO_2 found by 2 : 4-D	ThO_2 calc. on the total filaments	% of ThO_2 obtained from the filaments	No. of Detns.
I	0.0057 g	0.2850	0.79	3
	0.0082	0.2830	0.79	3
	0.0170	0.2850	0.79	3
	0.0198	0.2820	0.79	3
II	0.0115	0.2875	0.80	3
	0.0230	0.2875	0.81	3
	0.0289	0.2890	0.81	3
	0.0348	0.2900	0.81	3
III	0.0371	0.2853	0.80	4
	0.0314	0.2854	0.80	4
	0.0143	0.2860	0.80	4

From Table II it is evident that an average of 0.8% thoria can be recovered from the different samples of the filaments. The rest, therefore, was tungsten plus impurities like silica *etc.* This method, however, is not very satisfactory, for the determination and extraction of thorium in tungsten filaments, as the % of thorium in them is very low, and 2 : 4-D does not produce quantitative precipitation from very dilute solutions, *i.e.* from solutions of very low thorium concentrations, below 0.002 g per 20 ml. A large quantity of tungsten-free solution containing thorium must be concentrated to a very small volume to get the desired results. As no suitable method is avaible to check our results obtained with this reagent, the % of tungsten and thorium as determined agree well with the percentages in which these metals are generally present in the filaments. Although the method is simple enough when plenty of filament material is available, it cannot be used for residues of the size and quantity which we usually encounter.

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SUMMARY

2 : 4-Di- chlorophenoxyacetic acid can be used as a reagent for the determination and extraction of thorium present in industrial wastes like worn-out gas mantles and tungsten filaments. At a pH of 2.8 to 3 thorium gives a voluminous precipitate

with 2 : 4-D, which filters, washes, and ignites readily. The voluminous nature of the precipitate is advantageous in the detection and determination of the very small quantity of thorium present in the filaments. The % recovery of thorium from gas mantles and tungsten filaments is 89.5 and 0.8 respectively. The process can only be utilised for the extraction of thorium from the filaments if a huge quantity of such materials can be procured at a time.

RÉSUMÉ

L'acide 2.4-dichlorophénoxyacétique peut être utilisé comme réactif pour le dosage et l'extraction du thorium dans divers déchets industriels tels que masques à gaz usés et filaments de tungstène. Au pH de 2.8 à 3 le thorium donne un précipité volumineux avec ce réactif, précipité qui se filtre, se lave et se calcine facilement. Cet acide 2.4-dichlorophénoxyacétique (en raison du volume du précipité obtenu) permet de déceler et de doser les très faibles quantités de thorium présents dans les filaments. La teneur en thorium des masques à gaz et des filaments de tungstène va de 89.5 à 0.8% respectivement. Cette méthode ne peut être utilisée pour l'extraction du thorium des filaments que si une très grande quantité peut être procurée en une fois.

ZUSAMMENFASSUNG

Die 2.4-Dichlorophenoxyessigsäure kann als Reaktiv für die Bestimmung und Extraktion von Thorium in verschiedenen Industrieabfällen, wie gebrauchten Gasmasken und Wolframfilamenten gebraucht werden. Bei pH-Werten zwischen 2.8 und 3 gibt das Thorium mit diesem Reaktiv einen voluminösen Niederschlag. Dieser lässt sich leicht filtrieren, waschen und kalzinieren. Die 2.4-Dichlorophenoxyessigsäure (wegen des grossen Volumens des erhaltenen Niederschlages) erlaubt, sehr geringe Quantitäten von Thorium in Filamenten zu finden und zu dosieren. Der Gehalt von Thorium in Gasmasken und in Wolframfilamenten geht resp. von 89.5 bis 0.8%. Diese Methode kann nur für die Extraktion von Thorium aus Filamenten angewendet werden, wenn davon auf einmal eine grosse Quantität an Ausgangsmaterial beschafft werden kann.

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A SELECTIVE PROCEDURE FOR THE GRAVIMETRIC ESTIMATION OF URANIUM AS OXINATE USING COMPLEXONE AS MASKING AGENT

by

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The method for the estimation of uranium in the hexavalent condition by precipitation with oxine was first developed by F. HECHT AND W. REICH-ROHRWIG[1] and later modified by A. CLAASSEN AND J. VISSER[2], who observed that the method due to HECHT AND REICH-ROHRWIG gave low results owing to the solubility of uranyl oxinate in hot water. The difficulty was overcome by washing the precipitate with 0.04% oxine solution. In the present investigation the observation of CLAASSEN AND VISSER has been confirmed and the process described by them has also been slightly modified. The method, although a very important one for the estimation of uranium, in which the oxinate can be directly weighed as $UO_2(C_9H_6NO)_2C_9H_7NO$ after drying at 110° [3,4], is highly disadvantageous owing to the interference caused by large number of elements under the conditions of the experiment. Therefore, the object of the present investigation is to develop a selective method employing a suitable masking agent which will be able to mask the interfering elements without exerting any influence on the complete precipitation of uranium. Selecting complexone (disodium salt of ethylenediaminetetraacetic acid, as the masking agent, it has been found that between pH ranges 5-9 it has no masking action on uranium and that uranium can be quantitatively separated from Th, R.E. (Rare earths), Zr, Fe^{+3}, Al, Cu, Co, Ni, Zn, Cd, Pb, Bi, Mn and P_2O_5 by precipitation with oxine in a solution buffered with acetic acid and ammonium acetate (pH approximately 5.3) and also from V_2O_5, MoO_3 and WO_3 in ammoniacal medium (pH approximately 8.4).

EXPERIMENTAL

Reagents and standard solutions

Chemicals used were all of analytical grade.

Reagents: (a) 10% solution of complexone in water; (b) 4% solution of oxine in absolute alcohol; (c) 20% ammonium acetate solution; (d) 1 : 1 acetic acid; (e) ammonia solution, prepared by passing ammonia gas into cold water; (f) 0.01% oxine solution (1 ml 4% solution per 400 ml of water) as the wash liquid.

Standard solution: Nitrates of U, Th, R.E., Fe^{+3}, Al, Cu, Ni, Zr, Zn, Cd, Pb, Bi, Mn, Co, and alkali salts of P_2O_5, V_2O_5, MoO_3 and WO_3 were used for the preparation of their standard solutions.

Standardization of uranium solution

Uranium solution was standardized according to the following modified procedure. The result was also further checked by ammonium diuranate method.

A measured portion of the slightly acid solution was neutralized with ammonia to a permanent turbidity (yellow to methyl red indicator). The turbidity was then cleared by the addition of 1 ml of 1 : 1 acetic acid and this was followed by 25 ml of 20 % ammonium acetate solution to raise the pH of the solution to about 5.4. The solution was then diluted to 150-175 ml, heated to about 70°, and 5 ml of 4 % alcoholic solution of oxine were then added dropwise with stirring (about six times the amount of U). The beaker with the precipitate was then allowed to stand for a few minutes in a bath of water at room temperature (about 30°) — the solution being stirred occasionally, removed from the bath and allowed to cool to room temperature. The precipitate was filtered through a sintered glass crucible (No. 3) — washed thoroughly with warm 0.01 % oxine solution — dried at 110° for one hour and weighed.

Study of the pH range for complete precipitation of uranium in presence of complexone

A measured portion of uranium solution was neutralized (to yellow colour of methyl red indicator) after the addition of a measured amount of 10 % complexone solution. The pH of the solution was then altered by variation of the amount of acetic acid and ammonia, adding always the same amount (25 ml) of ammonium acetate solution. The pH of the first filtrate was measured with a Muirhead pH meter. The results are given in Table I.

It is clearly evident from the results in Table I that between pH ranges 5-9 complexone exerts no influence on the complete precipitation of uranium. At higher pH, less reagent may be used (results 12 and 15), but estimation at a pH not far below 5 can only be carried out with more reagent in presence of less complexone (result 3).

Separation from Th, R.E., Fe^{+3}, Al, Cu, Cd, Zn, Pb, Bi, Mn, Co and Ni

A measured portion of uranium solution containing the interfering element was neutralized (to yellow colour of methyl red indicator) after the addition of a measured amount of complexone solution. 1.1 ml acetic acid was then added followed by 25 ml ammonium acetate solution to raise the pH to about 5.3. The

TABLE I

No.	U taken in mg	Complexone solution added in ml	Reagent solution added in ml	U found in mg	pH	Error in mg
1	34.26	3	5	6.71	4.55	—27.55
2	34.26	3	5	33.92	4.75	—0.34
3	34.26	3	7.5	34.26	4.70	nil
4	34.26	10	7.5	33.02	4.70	—0.95
5	34.26	3	5	34.20	5.03	—0.06
6	34.26	10	5	34.14	5.00	—0.12
7	34.26	3	5	34.33	5.12	+0.07
8	34.26	10	5	34.26	5.15	nil
9	34.26	5	5	34.33	5.35	+0.07
10	34.26	10	5	34.30	5.30	+0.04
11	28.44	10	5	28.44	5.60	nil
12	34.26	10	4.5	34.20	6.00	—0.06
13	28.44	5	5	28.44	6.50	nil
14	34.26	10	5	34.26	7.85	nil
15	34.26	10	4.5	34.30	8.30	+0.04
16	34.26	3	5	34.30	8.60	+0.04
17	34.26	10	5	34.33	9.10	+0.07
18	13.71	10	5	13.78	5.50	+0.07
19	6.85	10	5	6.87	5.53	+0.02

TABLE II

No.	U taken in mg		Metal taken in mg	Complexone solution added in ml	U found in mg	Error in mg
1	28.44	Th	24.5	3	28.44	0.00
2	28.44	,,	49.0	3	28.37	—0.07
3	28.44	,,	98.0	3	28.44	0.00
4	34.26	,,	245.0	10	34.33	+0.07
5	28.44	R.E. (as oxide)	30.0	5	28.36	—0.08
6	34.26	,,	100.0	10	34.30	+0.04
7	34.26	Fe	12.50	10	34.26	nil
8	34.26	,,	15.0	10	34.40	+0.14
9	34.26	,,	17.5	10	34.86	+0.60
10	34.26	Al	28.0	10	34.30	+0.04
11	34.26	,,	42.0	10	34.33	+0.07
12	34.26	,,	50.0	10	35.54	+1.28
13	34.26	Cu	16.0	10	34.30	+0.04
14	34.26	,,	20.0	10	34.60	+0.34
15	28.44	Cd	27.0	5	28.36	—0.08
16	34.26	,,	100.0	10	34.33	+0.07
17	28.44	Zn	28.0	5	28.36	—0.08
18	34.26	,,	100.0	10	34.42	+0.16
19	34.26	Pb	100.0	10	34.20	—0.06
20	34.26	,,	400.0	10	34.20	—0.06
21	28.44	Bi	27.0	5	28.36	—0.08
22	34.26	,,	100.0	10	34.33	+0.07
23	28.44	Mn	27.5	5	28.36	—0.08
24	34.26	,,	100.0	10	34.46	+0.20
25	28.44	Co	25.0	5	28.50	+0.06
26	34.26	,,	100.0	10	34.40	+0.14
27	28.44	Ni	28.0	5	28.40	—0.04
28	34.26	,,	100.0	10	34.26	+0.10

subsequent procedure is the same as described under *Standardization of uranium solution.* Results are given in Table II.

Separation from zirconium

Procedure as described above was followed. Results are shown in Table III.

TABLE III

No.	U taken in mg	Zr taken in mg	Complexone solution added in ml	U found in mg		Error in mg
1	28.44	25.0	5	28.37		—0.07
2	34.26	25.0	10	34.33		+0.07
3	34.26	62.5	10	nil		—
4	34.26	100.0	10	nil		—
5	34.26	62.5	10	26.41	(kept overnight)	—7.85
6	34.26	62.5	10	25.64	(pH 5.6)	—8.62
7	34.26	75.0	10	34.20	(7 ml reagent)	—0.06
8	34.26	100.0	10	34.26	(9 ml reagent)	nil

Results (1-4) above clearly show that zirconium when present in excess of a certain quantity prevents precipitation of uranium with 5 ml of the precipitant. Standing over-night or raising the pH effected no improvement in the results (results 5 and 6). Satisfactory results were obtained with the addition of 1 ml excess of the reagent over that required to cause slight precipitation (results 7 and 8).

Separation from P_2O_5

A measured portion of uranium solution containing phosphate and sufficient nitric acid to prevent precipitation of uranyl phosphate was diluted to about 125 ml. 10 ml of complexone solution was then added followed by 7.5 ml of the oxine solution. The whole was heated to about 70°, neutralized with ammonia just to the yellow colour of thymol blue and the precipitation was then completed by dropwise addition of 25 ml ammonium acetate solution (to raise the pH to approximately 5.3) with constant stirring. The subsequent procedure is the same as described in previous separations. Results are given in Table IV.

TABLE IV

No.	U taken in mg	P_2O_5 taken in mg	U found in mg	Error in in mg
1	34.26	32.0	34.26	nil
2	34.26	64.0	34.33	+0.07
3	34.26	100.0	34.40	+0.14

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Separation from MoO_3, V_2O_5 and WO_3

A measured portion of uranium solution, containing molybdate, vanadate or tungstate and sufficient nitric acid to prevent formation of uranyl salts of the interfering acids, was diluted to about 100 ml. 10 ml of complexone and 10 ml of ammonium acetate solution were added one after another and the solution was then diluted to about 150 ml, heated to about 70° and neutralized with ammonia to the just pink colour of phenolphthalein. 5 ml of oxine solution was then added dropwise with constant stirring. The subsequent procedure was the same as described in previous separations. pH of the solution was varied with variation of the amount of ammonia. Results are shown in Table V.

TABLE V

No.	U taken in mg	MoO_3, V_2O_5 & WO_3 taken in mg	U found in mg	pH	Error in mg
1	34.26	MoO_3 — 50.0	34.60	8.30	+0.34
2	34.26	,, — 50.0	34.30	8.60	+0.04
3	34.26	,, — 75.0	34.33	8.65	+0.07
4	34.26	,, — 75.0	34.33	8.90	+0.07
5	34.26	V_2O_5 — 24.0	34.46	8.10	+0.20
6	34.26	,, — 24.0	34.26	8.30	nil
7	34.26	,, — 48.0	34.26	8.40	nil
8	34.26	,, — 48.0	34.30	8.60	+0.04
9	34.26	WO_3 — 42.0	34.46	8.10	+0.20
10	34.26	,, — 42.0	34.26	8.40	nil
11	34.26	,, — 63.0	34.40	8.45	+0.14
12	34.26	,, — 63.0	34.46	8.60	+0.20

CONCLUSION

From the experimental results above it may be concluded that uranium can be estimated in presence of quite a considerable amount of interfering elements using complexone as masking agent. Investigations are already in progress on the separation of uranium from mixtures and larger amounts of interfering elements especially Fe^{+3}, Al and Cu, and also on the development of a selective procedure for the colorimetric estimation by extraction of the oxinate with chloroform using the same masking agent. The results will be communicated in a subsequent paper.

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SUMMARY

The existing method for the estimation of U in hexavalent condition as oxinate has been slightly modified and the scope of complexone (disodium salt of ethylenediaminetetraacetic acid) as a masking agent to develop a selective method for its estimation in presence of interfering elements has been studied. It has been found that at pH ranges from 5-9 complexone exerts no influence on the complete precipitation of uranium and that uranium can be quantitatively separated from Th, R.E., Zr, Fe^{+3}, Al, Cu, Co, Ni, Zn, Cd, Pb, Bi, Mn and P_2O_5 by precipitation with oxine in a solution buffered with acetic acid and ammonium acetate (pH approximately 5.3) and also from V_2O_5, MoO_3 and WO_3 in ammoniacal medium (pH approximately 8.4).

RÉSUMÉ

La méthode de dosage de l'uranium(VI), comme oxinate a été légèrement modifiée et l'influence du complexon (sel disodique de l'acide éthylène-diaminotétraacétique ou EDTA) pour complexer les ions gênants, et rendre ainsi la méthode plus sélective, a été étudiée. Du pH 5 au pH 9 le complexon ne gêne pas la précipitation de l'uranium; ce dernier peut être alors séparé quantitativement de Th, T.R., Zr, Fe^{+3}, Al, Cu, Co, Ni, Zn, Cd, Pb, Bi, Mn et P_2O_5 par précipitation à l'oxine en solution tampon acide acétique — acétate d'ammonium (pH environ 5.3); il peut être séparé également de V_2O_5, MoO_3 et WO_3 en solution ammoniacale (pH environ 8.4).

ZUSAMMENFASSUNG

Die Methode zur Bestimmung von Uranium(VI) als Oxinat wurde leicht abgeändert, und der Einfluss von Komplexon untersucht (Dinatriumsalz der Ethylendiaminotetraessigsäure oder EDTA), um die störenden Ionen zu komplexieren und so die Methode selektiver zu gestalten. Im Bereiche der pH-Werte von 5 bis 9 stört das Komplexon die Ausfällung des Uraniums nicht. Dieses letzte kann also quantitativ von Th, S.E., Zr, Fe^{+3}, Al, Cu, Co, Ni, Zn, Cd, Pb, Bi, Mn und P_2O_5 getrennt werden durch Ausfällung mit Oxin in einer Pufferlösung von Essigsäure mit Ammoniumacetat (pH ungefähr 5.3). Es kann ebenfalls getrennt werden von V_2O_5, MoO_3 und WO_3 in ammoniakalischer Lösung (pH ungefähr 8.4).

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A RELATION BETWEEN R_F VALUES OF UNIDIMENSIONAL AND CIRCULAR PAPER CHROMATOGRAPHY

by

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In unidimensional paper chromatography, R_F values of substances found by either ascending or descending techniques are almost equal[1]. It has been observed, however, by RAO AND GIRI[2] and by CHAKRABORTY AND BURMA[3] that the R_F values in circular paper chromatography are higher than those in unidimensional paper chromatography. This was more convincingly demonstrated by CHAKRABORTY AND BURMA[4] who worked with different angular cuts of filter paper. The last named authors and also SAIFER AND ORESKES[5] pointed out the factors affecting reproducibility of measurements in circular paper chromatography. A complete review of the subject has recently been given by GANGULI[6]. STRAIN, SATO AND ENGELKE[7] analysed critically the $R_F^{(\text{Circ.})}$ values by circular paper chromatography of sugars observed by BERSIN AND MÜLLER[8] and found that $R_F^{\text{Circ.}\,2}$ is equal to R_F^{Linear}. It is the purpose of this investigation not only to give further experimental evidence in support of the above relation by working with different substances and different solvents, but also to adduce a theoretical basis for it.

EXPERIMENTAL

The following amino acids, sugars, spraying agents, solvents and paper have been used.

Amino acids — Arginine, lysine, serine, histidine, aspartic acid, glycine, threonine, glutamic acid, alanine, methionine, valine and leucine.

Sugars — Glucose, lactose, arabinose, maltose, mannose, galactose, xylose and rhamnose.

Spraying reagents — *For amino acids:* 0.2% ninhydrin in acetone.
For sugars: Aniline-diphenylamine-phosphate prepared according to the method of BUCHAN AND SAVAGE[9].

Solvents — (1) Phenol-water.
(2) Benzyl alcohol: acetic acid: water (100 : 20 : 26)[10].

Paper — Whatman No. 1 filter paper. For unidimensional paper chromatography, a filter paper sheet, 52 × 46 cm, and for circular paper chromatography, 18.5 cm diameter circular filter paper have been used.

METHODS OF PAPER CHROMATOGRAPHY

Unidimensional technique

The usual technique of unidimensional paper chromatography as described by CHAKRABORTY AND BURMA[11] by descending development has been followed, special care being taken to keep the temperature at 30° C ± 0.5° C. Amino acids and sugars are spotted in separate sheets on a line 7 cm apart from the longer side of the sheet at an interval of 3 cm. The sheets are then developed individually with the above mentioned solvents. After development they are allowed to dry in air and then sprayed with the proper spraying reagents.

Circular technique

The circular technique used is almost the same as that adopted by GIRI AND RAO[12]. The centre of the circular paper is found geometrically. It is then used as the master sheet to mark the centre of all the other pieces of paper used in a run. On the circumference of a concentric circle of 1 cm radius smaller circles of 4 mm diameter are drawn, on which the substances to be chromatographed are spotted. A rectangular paper strip, 2 × 1.5 cm, is folded lengthwise and inserted through a hole at the centre such that a 2 mm length projects on top. The circular sheet is then placed between two equal sized petri dishes of 16.5 cm diameter. The solvent is kept in a smaller petri dish placed inside the larger ones. The smaller dish contains always 20 ml of solvent for development. Care is taken to maintain the size of wick and length of the exposed wick constant, otherwise the R_F values are affected[5].

R_F values

Both the solvents were used for determining the R_F values of amino acids and sugars. The R_F values are calculated in two ways by recording the substance distance (A) from centre of spot or arc, and (B) from the frontal boundary of the spot or arc.

Firstly, R_F values are determined, applying the two methods, and calculations are made for the above relation in order to find out which of the two methods is more suitable for approaching the above relation. Then, in the subsequent experiments that method of determining R_F values is applied. Secondly, experiments are done in order to find out the proper conditions on which the approach to the above relation depends.

RESULTS

Table I records the R_F values of amino acids in phenol-water and benzyl-alcohol-acetic acid-water applying both the methods for the calculation of R_F values; squares of R_F values by circular technique are also indicated in the same table.

Table II records the R_F values of amino acids when the solvent fronts are allowed to travel (a) a distance in unidimensional method which is the square of the distance allowed in the circular method; (b) a distance not having any particular relation between the two; the squares of R_F values by circular technique thus obtained are also shown in this table.

Table III records the R_F values of sugars when solvent fronts are allowed to travel distances as above and squares of such R_F values by circular technique.

DISCUSSION

From Table I it is clear that when the R_F values are calculated considering the frontal boundary of spot or arc, the square of R_F values by circular technique approaches more closely the linear R_F values. The subsequent calculations of R_F values have therefore been made with reference to the frontal boundary of the spot or arc.

From the data presented in Tables II and III it is observed that whatever be the distance of solvent front the square of the R_F value calculated from circular technique always approaches the R_F value calculated from the unidimensional procedure. Moreover, this relation is obeyed both by the amino acids and the sugars. The same relation is verified by the data of BERSIN AND MÜLLER[8], with the solvent mixture, butanol-acetic acid-water.

The above experimentally realized relation, *viz.*, $(R_F^{\text{Circ.}})^2 = R_F^{\text{L}}$, where $R_F^{\text{Circ.}}$ and R_F^{L} are the R_F values according to the circular and unidimensional procedures respectively, may be obtained also on theoretical grounds in the following way:

Let r_1 and r_2 be the radial solute and solvent fronts. The volume, v_2, occupied by the solvent $= 4r_2^2df_2$, where
d is the thickness and
f_2 is the accommodation factor.
It is now assumed that the solvent moving the solute has a different accommodation factor, f_1, so that the volume, v_1, occupied by it $= 4r_1^2df_1$.

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TABLE I

R_F VALUES IN PHENOL-WATER AND BENZYL ALCOHOL-ACETIC ACID-WATER

Amino acids	Phenol-water						Benzyl alcohol-acetic acid-water					
	Calculated on the basis of frontal boundary of spot or arc			Calculated on the basis of centre of spot or arc			Calculated on the basis of frontal boundary of spot or arc			Calculated on the basis of centre of spot or arc		
	Unidimensional	Circular (c)	$(c)^2$	Unidimensional	Circular (c_1)	$(c_1)^2$	Unidimensional	Circular (c_2)	$(c_2)^2$	Unidimensional	Circular (c_3)	$(c_3)^2$
Arginine	0.58	0.75	0.562	0.52	0.67	0.448	0.065	0.26	0.067	0.058	0.24	0.057
Lysine	0.50	0.70	0.49	0.44	0.65	0.42	0.049	0.22	0.048	0.04	0.20	0.04
Serine	0.36	0.57	0.324	0.31	0.54	0.29	0.072	0.27	0.072	0.06	0.23	0.052
Histidine	0.63	0.80	0.64	0.56	0.77	0.592	0.078	0.28	0.078	0.065	0.24	0.057
Aspartic acid	0.15	0.37	0.134	0.12	0.32	0.104	0.11	0.32	0.102	0.09	0.28	0.078
Glycine	0.44	0.64	0.409	0.38	0.58	0.336	0.10	0.35	0.12	0.08	0.31	0.096
Threonine	0.52	0.72	0.518	0.47	0.66	0.435	0.13	0.34	0.11	0.10	0.30	0.09
Glutamic acid	0.31	0.56	0.313	0.23	0.43	0.184	0.11	0.32	0.10	0.08	0.29	0.084
Alanine	0.59	0.76	0.577	0.55	0.72	0.518	0.18	0.44	0.19	0.15	0.42	0.17
Methionine	0.80	0.90	0.81	0.72	0.87	0.756	0.42	0.64	0.409	0.39	0.61	0.37
Valine	0.78	0.88	0.77	0.76	0.87	0.756	0.39	0.62	0.384	0.37	0.59	0.348
Leucine	0.84	0.92	0.846	0.80	0.88	0.77	0.52	0.72	0.518	0.50	0.69	0.476

TABLE II

R_F VALUES OF AMINO ACIDS WHEN SOLVENT FRONT IS ALLOWED TO TRAVEL RESTRICTED DISTANCE

Amino acids	Phenol-water						Benzyl alcohol-acetic acid-water					
	Distance of solvent front						Distance of solvent front					
	Unidimensional 49 cm	36 cm	Circular 7 cm (c_1)	6 cm (c_2)	$(c_1)^2$	$(c_2)^2$	Unidimensional 49 cm	36 cm	Circular 7 cm (c_3)	6 cm (c_4)	$(c_3)^2$	$(c_4)^2$
Arginine	0.58	0.57	0.75	0.74	0.562	0.542	0.065	0.063	0.26	0.25	0.067	0.062
Lysine	0.50	0.50	0.70	0.70	0.49	0.49	0.049	0.048	0.22	0.23	0.048	0.05
Serine	0.35	0.34	0.56	0.55	0.313	0.302	0.072	0.07	0.27	0.28	0.072	0.078
Histidine	0.63	0.63	0.80	0.81	0.64	0.65	0.078	0.077	0.28	0.29	0.078	0.08
Aspartic acid	0.15	0.14	0.37	0.38	0.136	0.14	0.10	0.11	0.32	0.31	0.102	0.096
Glycine	0.44	0.42	0.64	0.65	0.409	0.42	0.10	0.11	0.35	0.33	0.12	0.108
Threonine	0.52	0.50	0.72	0.71	0.518	0.50	0.12	0.12	0.34	0.35	0.11	0.12
Glutamic acid	0.31	0.31	0.55	0.54	0.302	0.291	0.11	0.11	0.31	0.30	0.096	0.09
Alanine	0.58	0.56	0.76	0.75	0.577	0.58	0.18	0.18	0.43	0.42	0.18	0.176
Methionine	0.80	0.80	0.90	0.90	0.81	0.81	0.42	0.43	0.63	0.62	0.396	0.384
Valine	0.77	0.77	0.88	0.85	0.77	0.72	0.38	0.39	0.61	0.60	0.372	0.36
Leucine	0.84	0.83	0.92	0.90	0.84	0.81	0.51	0.52	0,72	0.72	0.51	0.518

TABLE III

R_F VALUES OF SUGARS WHEN SOLVENT FRONT IS ALLOWED TO TRAVEL RESTRICTED DISTANCE

Sugars	Phenol-water						Benzyl alcohol-acetic acid-water					
	Distance of solvent front						Distance of solvent front					
	Unidimensional 49 cm	36 cm	Circular 7 cm (c_1)	6 cm (c_2)	$(c_1)^2$	$(c_2)^2$	Unidimensional 49 cm	36 cm	Circular 7 cm (c_3)	6 cm (c_4)	$(c_3)^2$	$(c_4)^2$
Glucose	0.37	0.36	0.61	0.60	0.37	0.36	0.074	0.074	0.27	0.26	0.072	0.067
Lactose	0.34	0.33	0.58	0.59	0.33	0.34	0.038	0.035	0.19	0.19	0.036	0.036
Arabinose	0.52	0.52	0.72	0.71	0.518	0.504	0.13	0.14	0.35	0.34	0.12	0.12
Maltose	0.32	0.32	0.57	0.58	0.324	0.33	0.029	0.03	0.17	0.17	0.028	0,028
Mannose	0.45	0.44	0.66	0.67	0.435	0.44	0.12	0.11	0.35	0.34	0.12	0.11
Galactose	0.45	0.45	0.65	0.65	0.422	0.422	0.098	0.10	0.31	0.32	0.096	0.10
Xylose	0.45	0.44	0.67	0.67	0.448	0.44	0.17	0.18	0.41	0.42	0.168	0.176
Rahmnose	0.60	0.60	0.78	0.79	0.60	0.60	0.28	0.29	0.53	0.54	0.28	0.29

For the sake of comparison, let the volumes v_1 and v_2 of the solvent be supposed to spread to distances l_1 and l_2 in the unidimensional chromatography over a strip of paper of the same quality,

then $v_2 = l_2.b.d.f_2$

and $v_1 = l_1.b.d.f_1$, where b is the width of the strip.

Hence,

$$\frac{4r_1^2df_1}{4r_2^2df_2} = \frac{l_1.b.d.f_1}{l_2.b.d.f_2}$$

$$\text{or, } \frac{r_1^2}{r_2^2} = \frac{l_1}{l_2}$$

$$\text{or, } (R_F^{\text{Circ.}})^2 = R_F^{\text{L}}$$

This is the relation which has been thoroughly confirmed by experiments with amino acids and sugars.

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SUMMARY

1. R_F values of 12 amino acids were determined in phenol-water and benzyl alcohol-acetic acid-water using unidimensional and circular techniques of paper chromatography.

2. It has been observed that the square of circular R_F values (considering frontal boundary of solute) equals the linear R_F values, and this relation is valid for the amino acids as well as the sugars studied.

3. The relation is found to be independent of the distance traversed by the solvent in the case of both amino acids and sugars.

4. A theoretical support has been given to the experimental observations.

RÉSUMÉ

1. Les valeurs de R_F de 12 acides aminés ont été déterminées dans les milieux: eau-phénol et alcool benzylique — acide acétique — eau, au moyen des deux techniques (unidimensionnelle et circulaire) de chromatographie sur papier.

2. On constate que le carré des R_F circulaires est égal aux R_F linéaires; ceci est valable aussi bien pour les acides aminés que pour les sucres étudiés.

3. Cette relation est indépendante de la distance traversée par le solvant dans le cas des acides aminés et des sucres.

4. Des explications théoriques ont été données à ces observations expérimentales.

ZUSAMMENFASSUNG

1. Die Werte für R_F von 12 Aminosäuren wurden in folgenden Milieus bestimmt: Wasser Phenol und Benzylalkohol — Essigsäure — Wasser. Die Bestimmung erfolgte nach den zwei für die Papierchromatographie angewandten Verfahren (eindimensional und kreisförmig).

2. Man stellt fest, dass das Quadrat des kreisförmigen R_F gleich des linearen R_F ist. Dies gilt sowohl für Aminosäuren wie für die untersuchten Zucker.

3. Dieses Verhältnis ist unabhängig von der vom Lösungsmittel durchlaufenen Distanz im Falle der Aminosäuren und der Zucker.

4. Theoretische Erklärungen werden zu den experimentellen Beobachtungen gegeben.

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SÉPARATION BARYUM-STRONTIUM PAR CHROMATOGRAPHIE SUR CELLULOSE

II. CHROMATOGRAPHIE SUR POUDRE DE CELLULOSE

par

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INTRODUCTION

Après les séries d'essais d'orientation décrites dans la première partie, nous avions conclu que le plus grand facteur de séparation pour Ba^{+2} — Sr^{+2} était obtenu avec un mélange méthanol — HCl. Les conditions opératoires étant mieux définies sur une colonne de poudre de cellulose, nous nous sommes proposés d'étudier systématiquement ces mélanges en vue de l'obtention d'une séparation quantitative.

DISPOSITIFS EXPÉRIMENTAUX

Nous avons utilisé, pour les recherches préliminaires, une colonne constituée d'un tube de verre de 50 cm de long et de 10.8 mm de diamètre intérieur et remplie sur une hauteur de 40 cm.

Pour les séparations proprement dites, nous avons employé une colonne thermostatisée (24° C) constituée par un réfrigérant de Liebig démontable: diamètre intérieur du tube 9.8 mm, hauteur utile de la cellulose 40 cm.

Dans les deux cas, la colonne était alimentée à niveau constant au moyen d'un siphon plongeant au fond d'un flacon de Volhard. Le siphon est constitué par un capillaire à parois épaisses pour éviter de brusques variations de niveau lors de la mise en marche.

Les fractions éluées étaient recueillies de manière continue à l'aide d'un collecteur automatique commandé par une minuterie électrique.

SUBSTANCES, DÉTECTION ET MESURES

Lors des essais préliminaires, pour la recherche d'un éluant nous avions ^{89}Sr (53 jours) et nous avons détecté Ba (inactif) au rhodizonate. Les quantités mises en oeuvre (chlorures) ont varié entre 1100 et 250 μg, car la solubilité de $BaCl_2$ décroît rapidement avec la concentration de HCl et d'éther dans le méthanol.

Pour détecter le baryum au rhodizonate, nous avons trouvé préférable d'évaporer à sec les portions d'élution puis de les reprendre par 1-2 ml d'eau (limite de sensibilité $\sim 3\ \mu g$).

En opérant directement dans l'éluat, après tamponnage par l'hexaméthylènetétramine, la réaction est nettement moins sensible.

Les fractions contenant le strontium actif sont évaporées dans des cuvettes en cuivre rouge pour la mesure de l'activité au compteur G-M.

(b) Les séparations proprement dites ont été effectuées au moyen de produits d'activité spécifique élevée: ^{140}Ba et ^{90}Sr (produits de fission période 12.8 jours et 25 ans).* Par désintégration β, ces isotopes donnent respectivement ^{140}La (40 heures) et ^{90}Y (60 heures). Nous avons donc dû attendre l'équilibre radioactif (pratiquement 5 à 6 périodes c.-à-d. 10 à 15 jours) pour la mesure définitive de la séparation Ba-Sr.

PRÉPARATION DES COLONNES, MODE OPÉRATOIRE

(a) Nous avons, pour le premier groupe d'essais, chargé la colonne à sec avec de la poudre brute "Whatman" qualité B; nous y avons fait passer successivement 100 ml des réactifs et solvants suivants: HCl 4*N*, acétone, éther, méthanol. Nous avons échelonné les expériences dans l'ordre des concentrations croissantes en additif (HCl ou eau) et avant l'obtention d'une certaine séparation entre les pics, nous n'avons opéré que sur un élément à la fois.

(b) Les essais de séparation proprement dits ont été effectués au moyen de cellulose traitée avant le chargement de la colonne: digestion de quelques jours dans HCl 4*N*, lavages à l'eau distillée, à l'acétone, puis à l'éther. Pour garder la poudre traitée parfaitement blanche, il faut la laisser sécher à l'air à la température ordinaire; à l'étuve elle jaunit.

Dans chaque essai, on commence par mettre la colonne en régime en y faisant passer environ 60 ml du mélange éluant à l'essai; on introduit le mélange des chlorures de baryum et de strontium dissous dans 1-2 ml de l'éluant, on rince les bords du tube, puis lorsque la solution est entrée dans la colonne on commence l'élution en amorçant le siphon par une légère pression d'air insufflé par la branche latérale du flacon de Volhard.

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* D'après l'analyse spectrographique fournie avec les produits radio-actifs, la solution de ^{140}Ba (32 ml) contenait 20 μg de Ba et 25 μg de La. Au cours de nos essais nous y avons décelé la présence d'un composé organique sublimable (acide oxalique?). C'est pourquoi, et compte tenu de certaines perturbations observées avec cette solution, nous avons préféré dans la suite calciner au préalable le produit sur platine; nous avons cependant constaté qu'après une telle calcination, le baryum se redissolvait assez difficilement.

La solution de ^{90}Sr (1.7 ml) était normale en HNO_3 et le résidu d'évaporation était < 0.2 mg.

ESSAIS SYSTÉMATIQUES DE DIFFÉRENTS TYPES D'ÉLUANTS

Dans les Figs. 1, 2 et 3, nous avons résumé l'ensemble des résultats caractéristiques des essais faits avec trois types d'éluants. Nous avons caractérisé les bandes de la façon suivante:

^{89}Sr (mesures d'activité): indications du début, du maximum et du centième de l'activité du maximum (d'après les courbes d'élution).

Ba (inactif): indications des limites de la détection au rhodizonate et de la position approximative du maximum d'après l'aspect des précipités.

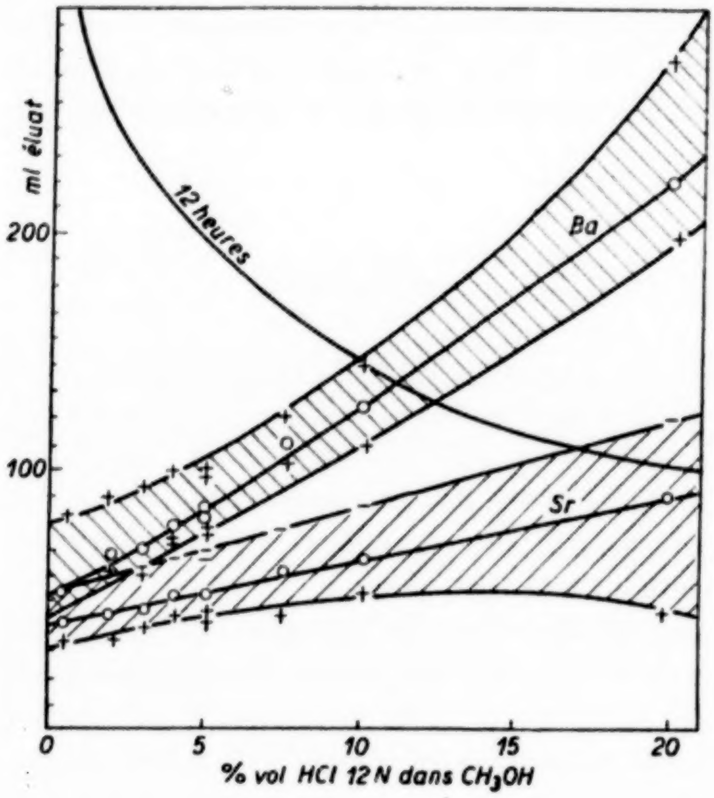

Fig. 1. Volume d'éluat en fonction du pourcentage en volume de HCl $12N$ en mélange avec le méthanol.

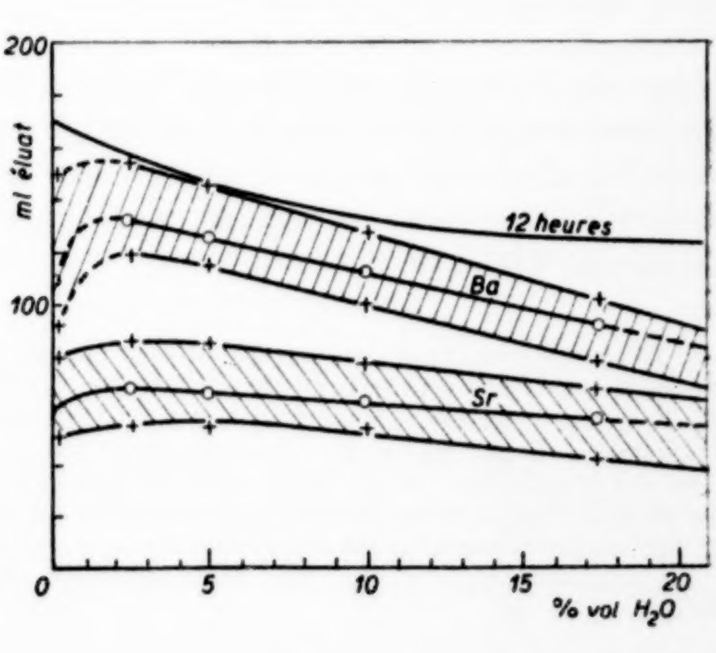

Fig. 2. Eluant: méthanol $1.2N$ en HCl gazeux + H_2O.

(a) *Eluant: méthanol + HCl 12N*

Sur la Fig. 1 nous avons représenté le volume d'éluat en fonction du pourcentage en volume de HCl 12*N* en mélange avec le méthanol. On peut considérer qu'à partir du mélange à 5 % les deux ions commencent à se séparer.

(b) *Eluant: méthanol 1.2N en HCl gazeux + H_2O*

Lors d'essais préliminaires, nous avions remarqué que l'addition d'eau à l'éluant diminuait le facteur de séparation, cette observation nous a incité à essayer des mélanges contenant moins d'eau que celle apportée par HCl 12*N* (75 % en volume). HCl gazeux se dissout aisément dans le méthanol, au moins jusqu'à une concentration correspondante à 8*N*; toutefois la solution ne se conserve pas très longtemps par suite d'une lente estérification de l'alcool; c'est pourquoi nous l'avons diluée avec du méthanol jusqu'à 1.2*N* en HCl et à cette solution de base, nous ajoutions des pourcentages variables d'eau.

La Fig. 2 résume les résultats obtenus avec ces mélanges. On voit que les meilleures séparations s'obtiennent avec des mélanges contenant seulement la moitié ou le tiers de l'eau qui serait normalement apportée par addition de HCl 12*N* nécessaire pour fixer la concentration en acide. Ces mélanges correspondent approximativement aux compositions $HCl.H_2O$ et $HCl.2H_2O$ en solution dans le méthanol.

(c) *Eluant: Méthanol-éther (v/v: 3/1) + HCl 12N*

Nous avons pensé qu'une addition d'éther à l'éluant permettrait de réduire la concentration en HCl qui risque de provoquer une hydrolyse trop rapide de la cellulose.

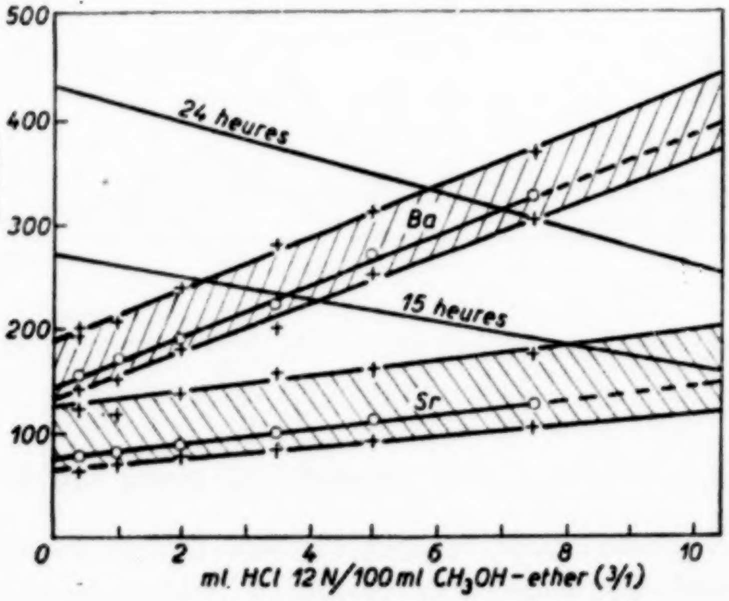

Fig. 3. Eluant: méthanol-éther (v/v : 3/1) + HCl 12*N*.

D'après les données rapportées sur la Fig. 3, on peut voir que l'on obtient déjà de bonnes séparations avec un mélange ne contenant que 2 ml de HCl 12*N* pour 100 ml du mélange de base méthanol-éther (3/1).

Remarque: Pour la plupart des courbes d'élution (Sr), nous observons un front assez raide et, après le maximum, une décroissance sensiblement exponentielle. Dans le cas de mélanges contenant beaucoup d'eau, l'aspect est inversé.

SÉPARATIONS PROPREMENT DITES DU BARYUM ET DU STRONTIUM

Les séparations rapportées ci-après ont toutes été obtenues avec le mélange éluant méthanol-éther-HCl 12*N* (75 : 25 : 5 en volume).

(a) *Avec entraîneurs (environ 200 μg)*

La Fig. 4 montre la séparation très nette obtenue dans ces conditions; elle met également en évidence l'étalement de la bande quand on passe du strontium au baryum; cet étalement est conforme à la théorie du phénomène: la partie hachurée à l'endroit du pic du strontium est obtenue en divisant les abscisses de la courbe du baryum par le rapport Vol Ba (max)/Vol Sr (max) = 3.7, qui n'est rien d'autre que le facteur de séparation.

La quantité maximum de $BaCl_2 \cdot 2H_2O$ est limitée par la solubilité dans le mélange: ∿ 275 γ/ml.

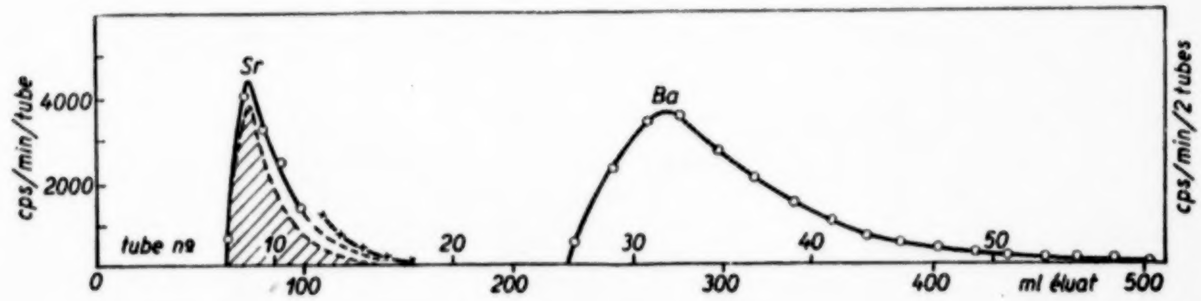

Fig. 4. Eluant: méthanol-éther-HCl 12*N* (75-25-5; v/v) avec entraîneurs.

(b) *Sans entraîneurs ($Ba^{+2} \leq 0.8$ μg; $Sr^{+2} \leq 0.001$ μg)*

Avant cet essai, nous avons eu soin de bien relaver la colonne avec 100 ml de HCl *N*/2, 100 ml de méthanol et 50 ml de l'éluant pour éliminer toute trace éventuelle de produits des essais antérieurs.

La Fig. 5 (a) nous montre encore une très bonne séparation; la courbe du strontium devient plus symétrique (faibles quantités).

La Fig. 5 (b) se rapporte aux mesures faites avant l'équilibre radioactif; on y remarque les pics de ^{90}Y et ^{140}La. L'activité sensiblement constante entre le pic du strontium et celui du baryum est due à la fraction du ^{140}La produite continuellement par ^{140}Ba au cours de l'élution. Nous avons attribué le tout petit pic juste après Sr^{+2} à une impureté non identifiée du baryum.

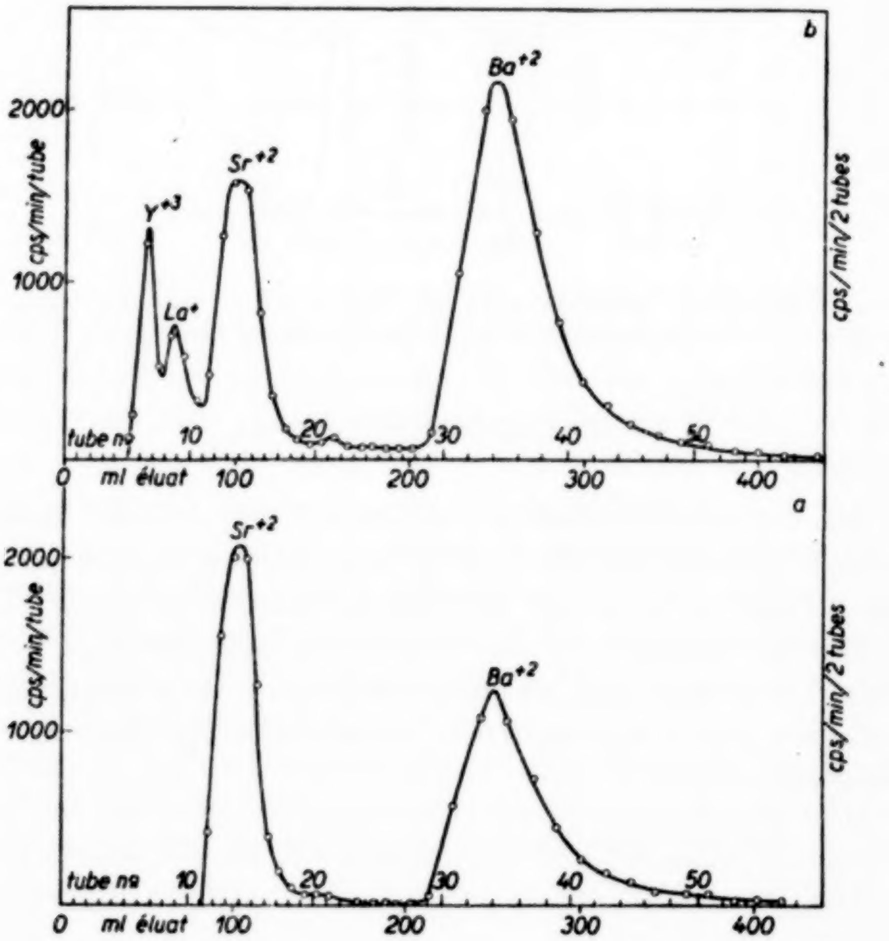

Fig. 5. Eluant: méthanol-éther-HCl 12N (75-25-5; v/v) sans entraîneurs.

(c) *Changement d'éluant (sans entraîneurs)*

En vue de réduire le temps et les volumes d'éluant nécessaires pour la récupération complète du baryum, nous avons changé d'éluant après la sortie du strontium, soit: méthanol-HCl 12N (100/5, v/v).

La Fig. 6 montre le progrès réalisé; le volume nécessaire pour l'élution du baryum est ramené de plusieurs centaines de ml à environ 50 ml.

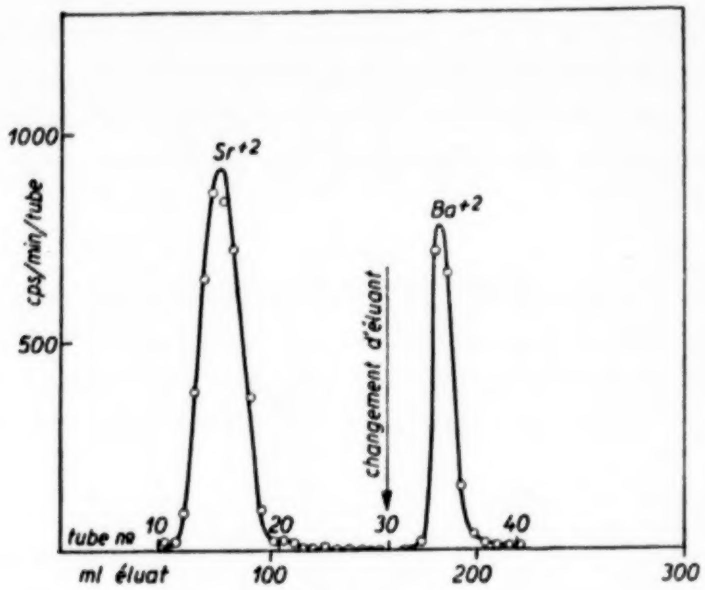

Fig. 6. Eluant: 1 méthanol-éther-HCl 12N (75-25-5; v/v)
2 méthanol-HCl 12N (100-5; v/v).

SÉPARATIONS CONNEXES

Au cours des essais préliminaires relatifs aux séparations baryum-strontium avec le mélange contenant de l'éther, nous avons obtenu de très bonnes séparations entre chaque produit actif et son produit de filation, à savoir: Y-Sr et La-Ba.

Nous donnons un exemple de ces séparations avec les Figs. 7 et 8, l'activité constante entre les pics ne doit pas être attribuée à un manque de résolution de la colonne, elle est due à la production continuelle d'yttrium et de lanthane au cours de l'élution.

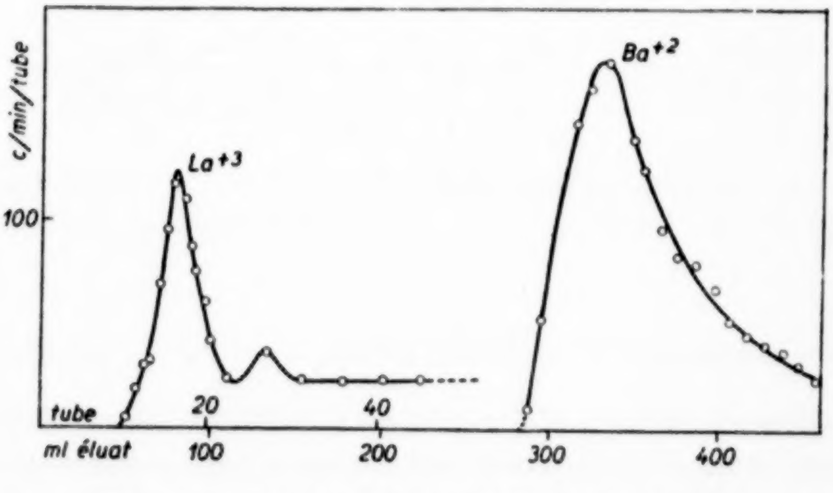

Fig. 7. Eluant: méthanol-éther-HCl 12N (75-25-5; v/v).

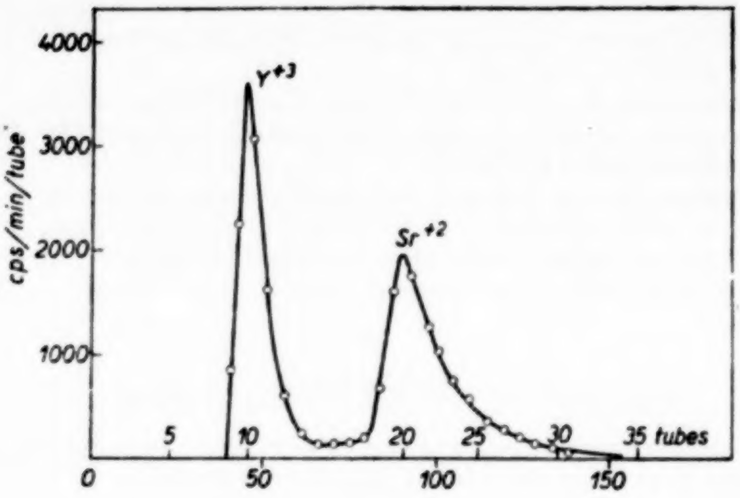

Fig. 8. Eluant: méthanol-éther-HCl 12*N* (75-25-5; v/v).

CONCLUSIONS

Les essais de chromatographie de partition sur une colonne de cellulose de 40 cm de longueur utile, nous permettent de tirer les conclusions suivantes:

1. Deux types de mélanges éluant donnent une bonne séparation Ba-Sr.
   (a) Méthanol 1.2*N* en HCl gazeux + 3 à 5 % d'eau en volume.
   (b) Méthanol-éther (3/1 : v/v) + 2 à 5 % de HCl 12*N*.
2. Le second mélange à 5 % en HCl a fourni de très bonnes séparations effectuées sur des quantités inférieures au milligramme.
3. Cette séparation fonctionne encore très bien avec des quantités de substances beaucoup plus faibles: $Sr^{+2} \leq 0.001$ μg, $Ba^{+2} \leq 1$ μg. Il ne paraît pas y avoir de limite inférieure.
4. En augmentant le pouvoir éluant du solvant après la sortie complète du strontium, il est possible de récupérer le baryum beaucoup plus rapidement.
5. Le mélange éluant convient également pour la séparation de quantités microchimiques d'yttrium et de lanthane respectivement du strontium et du baryum.

REMERCIEMENTS

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RÉSUMÉ

La recherche systématique d'une bonne séparation Ba^{+2}-Sr^{+2} sur colonne de poudre de cellulose nous a permis de sélectionner deux mélanges éluants:
(a) Méthanol 1.2*N* en HCl gazeux + eau (v/v : $100/_5$)
(b) Méthanol-éther-HCl 12*N* (v/v : 75-25-5)

Le second mélange nous a ensuite donné d'excellentes séparations aussi bien avec des quantités de l'ordre de 200 μg qu'avec des quantités nettement inférieures: Sr^{+2} $\leq$ 0.001 μg; Ba^{+2} $\leq$ 0.8 μg.

Enfin, en augmentant le pouvoir éluant du mélange après l'élution complète de Sr^{+2} (suppression de l'éther), nous avons réduit considérablement le temps et les volumes nécessaires pour le Ba^{+2}.

Cette étude a été faite au moyen des indicateurs radioactifs ^{140}Ba (12.8 jours) et ^{90}Sr (25 ans), et accessoirement nous avons pu montrer que le même éluant permet d'obtenir de bonnes séparations des isotopes ^{140}Ba et ^{90} Sr avec leurs produits de filiation β respectifs: ^{140}La (40 heures) et ^{90}Y (65 heures).

SUMMARY

The systematic investigation of a good Ba^{+2}-Sr^{+2} separation using a cellulose powder column has given us the choice of two eluants:

(a) Methanol 1.2*N* en HCl (gazeux) + water (v/v:100/5)

(b) Methanol-ether-HCl 12*N* (v/v:75-25-5).

The second one gave excellent separations, both in quantities of the order of 200 mg and in tracer amounts: Sr $\leq$ 0.001 μg-Ba $\leq$ 0.8 μg.

If we increase the eluting power of the solvent after the complete elution of Sr^{+2} (suppression of ether), we considerably reduce the time and volume needed for the Ba^{+2} elution.

This work was done with the help of radioactive isiotopes ^{140}Ba (12.8 days) and ^{90}Sr (25 years). At the same time, we found that the eluant used is also efficient for the separation of ^{140}Ba and ^{90}Sr from their respective decay products: ^{140} La and ^{0}Y (40h and 65h).

ZUSAMMENFASSUNG

Eine systematische Forschung für eine gute Trennung Ba^{+2}-Sr^{+2} durch eine Zellulose-Pulversäule erlaubt uns zwei Lösungs mittel auszuwählen:

(a) Methanol 1.2*N* HCl (gas) + Wasser (v/v : 100/5)

(b) Methanol-Äther-HCl 12*N* (v/v : 75-25-5)

Die zweite Mischung hat uns sowohl mit Mengen in der Grösse von 200 μg als auch mit sehr geringen Mengen (Sr^{+2} $\leq$ 0.001 μg, Ba^{+2} $\leq$ 0.8 μg vortreffliche Trennungen gegeben.

Wenn wir das Elutionsvermögen der Mischung nach der ganzen Sr^{+2}-Elution grösser machen (Auslassung von Äther), dann werden die Zeit und die Volumen für die Ba^{+2}-Elution beträchtlich kleiner.

Diese Arbeit wurde mit Hilfe der radioaktiven Isotopen durchgeführt ^{140}Ba (12.8 T.) und ^{90}Sr (25 J.); nebenbei konnten wir zeigen, dass dasselbe Elutionsmittel zu guten Trennungen der Isotopen und ihrer Filiationsprodukte ^{140}La (40 St.) und ^{90}Y (65 St.) führt.

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A MICRO-HETEROMETRIC DETERMINATION OF TRACES OF IRON (III) IN ALLOYS AND SALTS WITH α-NITROSO β-NAPHTHOL

by

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INTRODUCTION

Investigations of the determination of ferric iron with α-nitroso-β-naphthol are reported in the literature[1].

α-Nitroso-β-naphthol is an extremely useful reagent for the micro-heterometric determination of minute quantities of iron in alloys and in concentrated solutions of most of the common salts[1]. The sensitivity of this heterometric determination exceeds that of cobalt with α-nitroso-β-naphthol and also that of nickel with dimethylglyoxime. (The concentration of the analysed ferric iron was between $2 \cdot 10^{-4}M$ and $6 \cdot 10^{-5}M$.) In spite of this, the accuracy of the determination is of the same order as in the other heterometric titrations.

From the material presented it can be deduced that neither the maximum optical density value at the end-points of the titration, nor the accuracy, depends in any way on the character of the foreign metal present or on their concentrations. The numerical maximum density value depends only on the concentration of the iron in the analysed solution, and is proportional to this concentration if the other working conditions remain unchanged. This is of advantage, since the solution may be diluted to a concentration corresponding to a maximum optical density value appropriate to easy measurement, on the basis of one preliminary experiment. The heterometric determination of iron is most useful when coloured solutions are analysed, as the thiocyanate method is inapplicable.

The time required for a heterometric titration generally increases with decreasing concentration of the reacting components, and in our experiments it lasted up to one hour. The required time is probably equal for a water and a 50% alcoholic solution.

A considerable part of the titrations were carried out in salt solutions in which the percentage of iron was as low as 0.1% or even lower. In spite of this, the error was between zero and 3%.

As to the calculated molar ratio of iron to α-nitroso-β-naphthol at the end-point of the titration a ratio of 1 to 6 was surprisingly found. Similar titrations were made with $Fe^{III}NH_4(SO_4)_2.12H_2O$ but this ratio always remained unchanged. This exceptional behaviour could not be explained by us and requires further clarification.

EXPERIMENTAL

The same apparatus and procedure were used as in previous heterometric investigations. All titrations were carried out at 20° C. A red filter was used. No additional filters were used, even in the presence of concentrated solutions of chromium or nickel.

Reagents

All reagents used were either analytical reagents or chemical pure. α-Nitroso-β-naphthol was a British Drug House "spot test" reagent. The iron chloride or ferric ammonium sulphate used, were prepared from molar stock solutions which were diluted to the desired concentrations. The final solutions were acidified with HCl or HNO_3 to give an 0.01*N* acid solution. Such solutions of iron, even though very dilute, remained unchanged for a long period.

RESULTS

a) *In the absence of foreign metals*

Table I is a compilation of experiments carried out in the absence of foreign cations. Three different concentrations of iron were used for the titrations. A comparison of experiments 1, 7 and 10, shows that the maximum density values obtained are approximately proportional to the amount of iron used for the analysis. On the other hand (exps. 7 and 10) there is no noticeable difference in the density values obtained when different concentrations of α-nitroso-β-naphthol are used for the titration. However, if the analysed water solution of iron is replaced by a 50% alcoholic solution, using the *same* amount of iron, the maximum density value is three times as high (exps. 7 and 14). (It is interesting to note that the same behaviour was observed with cobalt and α-nitroso-β-naphthol.) The character of the precipitate remains unchanged under different working conditions (exps. 1-4). In the presence of phosphoric acid (exp. 5) no definite end-point was obtained and the density continued to rise after the calculated end-point. In the presence of trisodium citrate or disodium tartrate (exps. 12 and 13) no precipitation occurred. The addition of varied amounts of acetic acid had no influence on the values of the maximum density (exps. 8 and 9, 15 and 16) obtained in water or 50% alcoholic solution. The results obtained with HCl in alcohol showed reduced maximum density values (exps. 18 and 20).

TABLE I

Composition: 5 ml aM $FeCl_3$ (0.01N HCl) + 15 ml supplements + x ml $\alpha\beta$ bM.* Temp. = 20° C Filter: red

Exp. nos.	Supplements	Molarity		Iron in mg	x ml		Initial precip. at ml	Maxim. optic. density	Approx. titration time in min	Error		
		$\alpha\beta_{(b)}$	$Fe_{(a)}$		content	found				%	γ	γ/ml
1	15 ml H_2O	0.01	0.0008	0.223	2.40	2.42	0.0	1.03	34	0.9	2.1	0.105
2	2 ml NH_4NO_3 2N + 13 ml H_2O	0.01	0.0008	0.223	2.40	2.48	0.0	1.0	55	+3.6	8.8	0.44
3	1 ml CH_3COOH M + 14 ml H_2O	0.01	0.0008	0.223	2.40	2.43	0.0	0.96	41	+1.3	3.1	0.15
4	2 ml HCl 0.1N + 13 ml H_2O	0.01	0.0008	0.223	2.40	2.42	0.0	0.96	25	+0.9	2.1	0.10
5	1 ml H_3PO_4 0.1M + 14 ml H_2O	0.01	0.0008	0.223	2.40	> 3.8	0.4	∞0.76	25			
6	10 ml alc. + 5 ml H_2O	0.01	0.0008	0.223				high				
7	15 ml H_2O	0.0025	0.00025	0.07	3.0	2.88	∿0.6	0.30	56	—4.0	3.0	0.15
8	1 ml CH_3COOH 0.1M + 14 ml H_2O	0.0025	0.00025	0.07	3.0	2.90	0.4	0.42	65	—3.3	2.3	0.11
9	1 ml CH_3COOH M + 14 ml H_2O	0.0025	0.00025	0.07	3.0	2.90	0.4	0.31	60	—3.3	2.3	0.11
10	15 ml H_2O	0.0050	0.00025	0.07	1.5	1.47	0.0	0.34	58	—2.0	1.4	0.07
11	1 CH_3COOH M + 14 ml H_2O	0.0050	0.00025	0.07	1.5	1.46	0.0	0.27	45	—2.7	2.0	0.01
12	1 ml Na_3-citrate 0.2M + 14 ml H_2O	0.005	0.0005	0.14			∞	0.0				
13	1 ml Na_2-tartrate 0.2M + 14 ml H_2O	0.005	0.0005	0.14			∞	0.0				
14	5 ml H_2O + 10 ml alc.	0.0025	0.00025	0.07	3.0	3.06	0.2	0.98	74	+2.0	1.4	0.07
15	1 ml CH_3COOH 0.1M + 10 ml alc. + 4 ml H_2O	0.0025	0.00025	0.07	3.0	2.97	0.2	0.78	67	—1.0	0.7	0.04
16	1 ml CH_3COOH M + 4 ml H_2O + 10 ml alc.	0.0025	0.00025	0.07	3.0	3.0	∿0.4	0.76	66	0.0		
17	5 ml H_2O + 10 ml alc.	0.005	0.00025	0.07	1.5	1.56	0.2	0.60	23	+4.0	2.8	0.1
18	1 ml HCl 0.1N + 4 ml H_2O + 10 ml alc.	0.0025	0.00025	0.07	3.0	3.13	0.0	0.29	65	+4.3	3.0	0.2
19	2 ml NH_4NO_3 2N + 3 ml H_2O + 10 ml alc.	0.0025	0.00025	0.07	3.0	2.80	∿0.4	0.44	75	—6.6	4.6	0.2
20	1 ml HCl 0.1M + 4 ml H_2O + 10 ml alc.	0.0025	0.00025	0.07	3.0	3.08	1.4	0.43	50	+2.7	2.0	0.1

* $\alpha\beta$ = α-nitroso-β-naphthol

b) *In the presence of foreign metals*

Table II and Fig. 1-2. contain the results of titrations of iron which were carried out in the presence of foreign cations. Parallel titrations were made in the absence (there was always a small quantity of HCl since the iron solution used

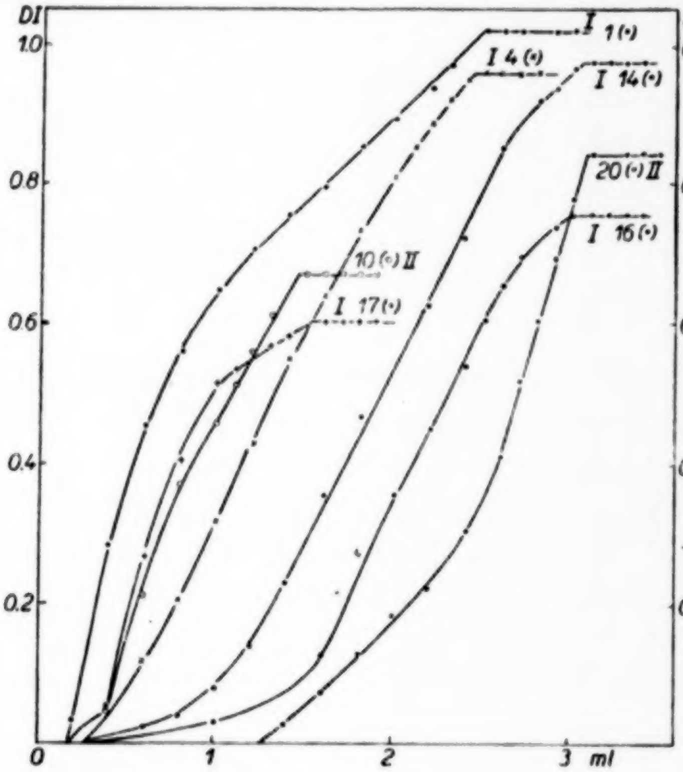

Fig. 1. Titration of iron with α-nitroso-β-naphthol in the presence of various salts.

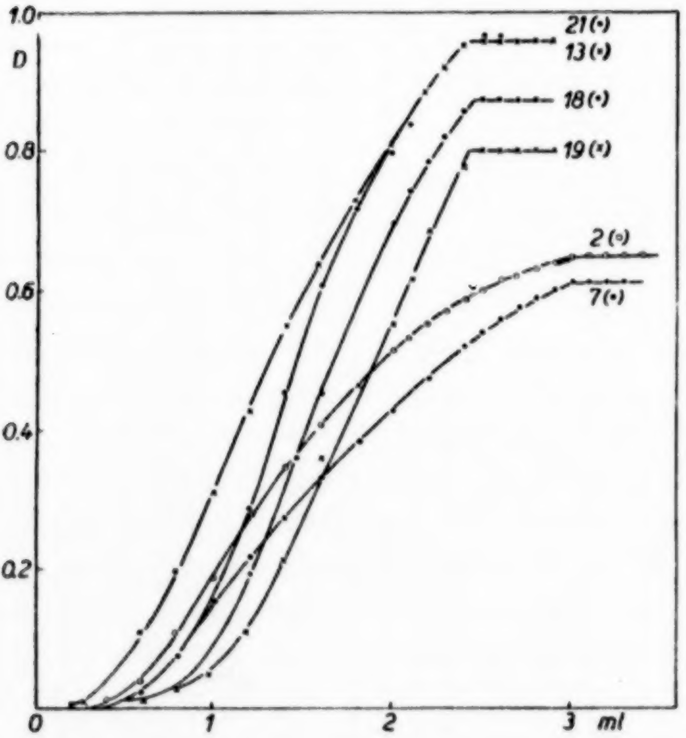

Fig. 2. Titration of iron with α-nitroso-β-naphthol in the presence of various salts.

TABLE II

Composition: 5 ml $FeCl_3$ a*M* (0.01 *N* HCl) + 15 ml supplements + *x* ml *αβ* * b*M* Temp. = 20° C. Filter: red.

Exp. no.	Supplements	mg supplement metal	% Fe	Iron in mg	Molarity		*x* ml		Initial precip. at ml	Maxim optical density value	Appro. titrat. time in min	Error		
					αβ (b)	Fe (a)	Content	found				%	*γ*	*γ*/ml
1	15 ml H_2O	—	—	0.223	0.01	0.0008	2.40	2.42	0.0	1.03	34	+0.8	1.8	0.1
2	4 $CaCl_2$ *M* + 11 ml H_2O	160.32	0.1	0.14	0.005	0.0005	3.00	3.00	0.2	0.65	35	0.0		
3	4 ml $CaCl_2$ 2*M* + 11 ml H_2O	320.56	0.04	0.14	0.005	0.0005	3.00	2.90	0.2	0.69	45	—3.3	4.6	0.2
4	4 ,, $BaCl_2$ *M* + 11 ,, ,,	550.68	0.03	0.14	0.005	0.0005	3.00	3.08	0.2	0.57	45	+2.7	3.7	0.2
5	8 ,, $BaCl_2$ *M* + 7 ,, ,,	1098.9	0.01	0.14	0.005	0.0005	3.00	3.06	0.2	0.56	60	+2.0	2.8	0.1
6	2 ,, $MgSO_4$ *M* + 13 ,, ,,	48.64	0.14	0.07	0.0025	0.00025	3.00	3.06	0.2	0.29	60	+2.0	1.4	0.07
7	4 ,, $MgCl_2$ *M* + 11 ,, ,,	97.28	0.1	0.14	0.005	0.0005	3.00	3.00	0.4	0.62	45	+0.0	0.0	0.0
8	4 ,, $ZnSO_4$ *M* + 11 ,, ,,	261.52	0.05	0.14	0.005	0.0005	3.00	3.10	0.2	0.65	70	+3.3	4.6	0.2
9	4 ,, $AlCl_3$ *M* + 11 ,, ,,	107.88	0.1	0.14	0.005	0.0005	3.00	2.82	0.2	0.59	33	—5.9	8.2	0.4
10	1 ,, $Cr(NO_3)_3$ *M* + 14 ml H_2O	52.01	0.27	0.14	0.005	0.0005	3.00	2.90	0.2	0.53	52	—3.3	4.6	0.2
11	1 ,, $CdSO_4$ *M* + 14 ,, ,,	112.41	0.12	0.14	0.005	0.0005	3.00	2.90	0.2	0.62	52	—3.3	4.6	0.2
12	2 ,, $Pb(NO_3)_2$ *M* + 13 ,, ,,	414.42	0.034	0.14	0.005	0.0005	3.00	3.10	0.2	0.67	45	+3.3	4.6	0.2
13	2 ,, HCl 0.1 *M* + 13 ,, ,,			0.223	0.01	0.0008	2.40	2.42	0.2	0.96	25	+0.8	1.8	0.1
14	2 ,, HCl 0.1 *M* + 4 ml $Ca(NO_3)_2$ *M* + 9 ml H_2O	160.32	0.13	0.223	0.01	0.0008	2.40	2.44	0.2	0.96	29	+1.6	3.6	0.2
15	2 ml HCl 0.1 *M* + 4 ml $MgCl_2$ *M* + 9 ml H_2O	97.28	0.23	0.223	0.01	0.0008	2.40	2.46	0.4	0.85	36	+2.4	5.4	0.3
16	2 ,, HCl 0.1 *M* + 8 ,, $ZnSO_4$ *M* + 5 ,, ,,	523.04	0.04	0.223	0.01	0.0008	2.40	2.42	0.2	0.98	34	+0.8	1.8	0.1
17	2 ,, HCl 0.1 *M* + 4 ,, $MnCl_2$ *M* + 9 ,, ,,	219.72	0.10	0.223	0.01	0.0008	2.40	2.42	0.2	0.96	30	+0.8	1.8	0.1
18	2 ,, HCl 0.1 *M* + 8 ,, $MnCl_2$ *M* + 5 ,, ,,	439.44	0.05	0.223	0.01	0.0008	2.40	2.44	0.4	0.88	17	+1.6	3.6	0.2
19	2 ,, HCl 0.1 *M* + 4 ,, $Ni(NO_3)_2$ *M* + 9 ,, ,,	234.76	0.09	0.223	0.01	0.0008	2.40	2.44	0.2	0.80	40	+1.6	3.6	0.2
20	2 ,, HCl 0.1 *M* + 4 ,, $AlCl_3$ *M* + 9 ,, ,,	107.88	0.20	0.223	0.01	0.0008	2.40	2.42	0.2	0.87	30	+0.8	1.8	0.1
21	2 ,, HCl 0.1 *M* + 8 ,, $AlCl_3$ *M* + 5 ,, ,,	215.76	0.10	0.223	0.01	0.0008	2.40	2.44	0.2	0.96	33	+1.6	3.6	0.2
22	2 ,, HCl 0.1 *M* + 1 ,, $Cr(NO_3)_3$ *M* + 12 ,, ,,	52.01	0.42	0.223	0.01	0.0008	2.40	2.44	0.0	0.87	36	+1.6	3.6	0.2
23	2 ,, HCl 0.1 *M* + 2 ,, $Cr(NO_3)_3$ *M* + 11 ,, ,,	104.02	0.2	0.223	0.01	0.0008	2.40	2.40	0.0	0.87	50	0.0		
24	2 ,, HCl 0.1 *M* + 1 ,, Na_2CrO_4 *M* + 12 ,, ,,	52.01	0.42	0.223	0.01	0.0008	2.40	2.35	0.2	0.64	32	—2.0	4.4	0.2
25	2 ,, HCl 0.1 *M* + 1 ,, Na_2MoO_4 0.1 *M* + 12 ml H_2O			0.223	0.01	0.0008	>3.0		0.2	∞0.15				
26.	2 ,, HCl 0.1 *M* + 1 ,, Na_2WO_4 0.1 *M* + 12 ml H_2O			0.223			>3.0	∞0.77	0.2					

* = α-Nitroso-β-Naphthol

was acidified to 0.01N with HCl) and in the presence of added HCl. No complexing agents were used as no interferences by foreign metals were encountered.

It seems that the physical state of the precipitate of iron with α-nitroso-β-naphthol is entirely unaffected by the concentrated salt solutions present (exps. 2-12 and 13-24). Each series gives its maximum density value, which depends only on the amount of iron that was analysed being proportional to these amounts.

The percentage of iron present depends of course on the atomic weight of the foreign metal. Thus, in a solution of barium, 0.01% iron could be determined with an error of 2% (exp. 5). In a lead solution with a content of 0.03% iron, the error was 3.3%. In calcium (exp. 3) or zinc (exp. 16) the iron content was 0.04%. In manganese (exp. 18) the percentage was 0.05 and the error was 1.6%. 0.1% of iron in nickel or aluminium could be analysed with an error of 1.6%.

There is probably no limit to the amount of foreign metal which can be present and the percentage of iron can still be much lower than that determined in our experiments.

Method

20 ml of solution in water which contains 0.07–0.2 mg of ferric iron and 2 ml 0.1N HCl are titrated heterometrically with a 0.01M–0.005M alcoholic solution of α-nitroso-β-naphthol. The titration lasts about one hour and the error is 0.0–4%.

SUMMARY

Ferric iron constituting approximately 0.01% — 0.1% may be determined by a heterometric titration with α-nitroso-β-naphthol. The solution may contain 99.9% or more of calcium, barium, magnesium, aluminium, chromium, manganese, nickel, cadmium or lead salts. No previous separation is necessary. The α-nitroso-β-naphthol is dissolved in alcohol. The analysed solution must be acidified. No complexing agents are necessary. Citrate or tartrate must be absent. The maximum optical density values which are obtained at the end of the titration are proportional to the amount of iron which is analysed. These maximum values are entirely unaffected by the concentrated salt solutions. The heterometric sensitivity of the reaction between iron and α-nitroso-β-naphthol is three times higher in 50% alcoholic solution than in water. The titration takes about one hour. The error is 0.0–4%.

RÉSUMÉ

Le fer ferrique (environ 0.01%-0.1%) peut être déterminé par titration hétérométrique avec l'α-nitroso-β-naphtol. La solution peut contenir $\geqslant$ 99.9% de sels de calcium, baryum, magnésium, aluminium, chrome, manganèse, nickel, cadmium et plomb. Aucune séparation préalable n'est nécessaire. L'α-nitroso-β-naphtol est dissous dans l'alcool. La solution à analyser doit être acidifiée; les agents complexants ne sont pas nécessaires. Le citrate et le tartrate doivent être absents. Les valeurs de la densité optique maximum obtenues en fin de titration

sont proportionelles aux quantités de fer analysé. Ces valeurs ne sont guère influencées par les concentrations en sels de la solution.

La sensibilité de la réaction fer-α-nitroso-β-naphtol est trois fois plus grande dans l'alcool à 50% que dans l'eau. La titration dure une heure environ. L'erreur est de 0.0–4%.

ZUSAMMENFASSUNG

Eisen (III) welches 0.01%-0.1% der Analyse ausmacht, kann mit α-Nitroso-β-Naphtol heterometrisch titriert werden. Die Lösung kann 99.9% oder mehr Salze des Calcium, Barium, Magnesium, Aluminium, Chrom, Mangan, Nickel, Cadmium oder Blei enthalten. Eine vorherige Trennung ist nicht notwendig. Das α-Nitroso-β-Naphtol wird in Alkohol gelöst. Die zu analysierende Lösung muss angesäuert werden. Der Zusatz von Metall-Komplexbildnern ist überflüssig. Citrate oder Tartrate dürfen nicht zugegen sein. Die im Maximumpunkt gefundene optische Dichte ist dem Eisengehalt proportional. Sie ist von der gegenwärtigen Salzkonzentration unbeeinflusst. Die heterometrische Empfindlichkeit der Reaktion von Eisen und α-Nitroso-β-Naphtol ist die dreifache in 50%ger alkoholische Lösung. Die Titration dauert etwa eine Stunde. Fehler 0.0–4%.

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A RAPID METHOD FOR THE DETERMINATION OF COPPER IN MINERAL OILS

by

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The determination of inorganic materials in petroleum products has always been difficult due to the large amount of organic material involved. The usual method for metals present in oil has been to burn the oil and determine the metal oxide present in the ash. When quantities in the microgram range have to be determined the difficulties increase as larger sample weights are necessary.

The oxidation of oils, and of transformer oil in particular, is known to be catalysed by microgram quantities of copper. Emphasis has therefore been placed on the determination of copper in transformer oils from service and oils undergoing laboratory oxidation tests.

In lubricating oils copper contamination is often taken as indicative of bearing attack and incipient failure.

The standard methods for the determination of copper[1,2] involve controlled combustion of the oil and determination of the copper in the ash by a colorimetric method. These methods are tedious and large errors can arise due to loss of sample during combustion and also to the large blanks caused by copper present in the reagents.

Modifications of these methods have been largely confined to the method of separating the copper from the oil. Various acid extraction methods have been proposed[3,4,5], and an Ion Exchange method[6]. Most of these methods involve chemical oxidation of residual organic material and colorimetric determination of copper with sodium diethyldithiocarbamate except ASSAF[5] who uses dithizone.

The methods are still tedious and the large reagent blanks limit the accuracy. Generally only small sample weights can be conveniently handled by these methods.

BARNEY[7] advocates a spectrographic method for determining copper in lubricating oil using oil impregnated electrodes with a spark discharge.

The method described in this paper overcomes many of the disadvantages of the previous methods. It is carried out with simple apparatus, is rapid (four simultaneous determinations can be done in 50 minutes) and, due to the use of large samples (up to 100 g) more accurate.

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The accuracy of the method is enhanced by the use of 2,2′-Diquinolyl[8,9], a sensitive and specific reagent for copper. At pH values greater than 3 this reagent gives with copper in the cuprous state a violet coloured complex. Furthermore the reagent solution is stable, and no protective colloid is necessary to stabilize the coloured complex.

EXPERIMENTAL

Consideration of the problem led to the belief that acetic acid would supply a suitable pH value for the use of cuproine and at the same time be sufficiently acidic to extract the copper from the oil.

Experiment showed that when glacial acetic acid was shaken with an oil containing copper in solution the copper was extracted into the acid layer, as after addition of solution of hydroxylamine hydrochloride and cuproine in methylated spirit, the violet coloured complex was formed.

It was felt that this might provide a satisfactory basis for a direct extraction method for soluble copper in transformer oil.

Accordingly a calibration curve for the Spekker photoelectric absorptiometer was prepared from a standard copper solution.

When the assay of an oil containing known amounts of copper in solution (prepared by weighing pure copper naphthenate (6.92% copper) into the oil) was attempted several difficulties arose:

(a) there was insufficient volume of extracting solution to separate completely from the oil,

(b) the extracting solution floated on the oil,

(c) the coloured extract was not clear due to contamination with traces of oil.

These difficulties were successively overcome by the following modifications:

(a) pure methylated spirits was added to increase the quantity of the extracting solution,

(b) petroleum spirit (a light petroleum fraction complying with B.S. 148: 1951 appendix B) was added to lower the specific gravity of the oil so that it floated on the extracting solution,

(c) a small quantity of benzene was added to clear the coloured extracts before final dilution and measurement on the Spekker.

Despite these modifications only about 90% of the added copper was recovered.

It was thought that this low recovery might be due to the acetic acid being insufficiently strong to extract all the copper from the added naphthenate.

Replacement of the acetic acid with a mineral acid was next tried. As removal of traces of organic matter by heating was not contemplated, hydrochloric acid was chosen. In view of the rapid separation of methylated spirit from the diluted oil, hydrochloric acid diluted with methylated spirits was first tried.

It was felt that extraction of the coloured complex from the solution in which it was formed would be a considerable improvement. The work of LUKE[10] and GAHLER[11] showed that chloroform was a suitable solvent for the 2;9-dimethyl-1;10-

phenanthroline (neocuproine) complex. Accordingly the extraction with chloroform was tried on the cuproine complex, the coloured complex was found to be rapidly and almost completely removed in a single extraction.

In the next series of experiments the oil, diluted with petroleum spirit, was twice shaken with small quantities of the 10% hydrochloric acid in methylated spirit and the acid layers run off into another separating funnel.

Sufficient sodium acetate and hydroxylamine hydrochloride solutions were added to buffer the solution to about pH 4 and to reduce the copper to the cuprous state. Finally, cuproine solution was added and the violet coloured complex extracted with two successive portions of chloroform. The chloroform extract was run into a graduated flask and diluted with methylated spirit. This method repeatedly produced clear solutions for absorptiometric measurement.

A calibration graph utilizing the chloroform extraction technique was prepared. The straight line obtained showed that Beers' Law was obeyed.

When this technique was applied to a transformer oil to which known amounts of copper in the form of the naphthenate had been added it was found to yield results showing excellent recovery of the added copper. Furthermore it was found to be a very rapid and easy procedure, the method working satisfactorily with quantities of oil ranging from 1 g to 100 g, depending on the amount of copper present.

FINAL METHOD

Reagents

All reagents of A.R. quality.

10% Hydrochloric Acid — 10 ml concentrated hydrochloric acid added to 90 ml pure methylated spirit or alcohol.

30% Sodium Acetate — dissolve 30 g sodium acetate (anhydrous) in 100 ml distilled water.

10% Hydroxylamine hydrochloride — dissolve 10 g hydroxylamine hydrochloride in 100 ml distilled water.

0.10% 2,2′-Diquinolyl (Cuproine) — dissolve 0.10 g cuproine in 100 ml methylated spirit or alcohol.

Stock Copper Solution — dissolve 1 g electrolytic copper in aqua regia, evaporate to dryness. Extract with 20 ml 1 : 1 dilute hydrochloric acid and dilute to 1 litre with distilled water. This contains 1 mg copper per ml.

Standard Copper Solution (10 µg per ml). Prepare daily from stock copper solution by dilution of 10 ml stock copper solution to 1 litre with distilled water.

Petroleum (Sludge) Spirit to B.S. 148/1951 Appendix B, Pure Petroleum Ether (60°-80° Bp) or *n*-heptane.

Methylated (Industrial) spirit or Pure Alcohol.

Calibration

To cover the range 0 μg to 100 μg of copper 0, 1, 2, 3-10 ml of the standard copper solution was pipetted into small separating funnels. 20 ml of 10% hydrochloric acid, 10 ml each of 30% sodium acetate and 10% hydroxylamine hydrochloride solutions were added and the funnels well shaken. 5 ml of 0.10% cuproine was added and the funnels shaken. The purple colour formed was extracted by the addition of 10 ml chloroform and the extract was run into a 50 ml graduated flask. The extraction was repeated with a further 5 ml chloroform, the extracts combined and diluted to 50 ml with methylated spirit. (Use alcohol when copper-free methylated spirit is not obtainable.) The absorption was measured on a Spekker Absorptiometer using 4 cm cells, Ilford Spectrum Yellow Green No. 605 filters and a water setting of 1.0. When the blank was deducted and the results plotted a straight line graph resulted.

Determination

A quantity of the oil under examination (10-100 g) was weighed out into a suitable sized separating funnel and diluted with an equal volume of petroleum spirit. 10 ml 10% hydrochloric acid was then added and the funnel shaken and after separation the acid layer run into a small separating funnel (100 ml size). A further 10 ml of acid was added and the procedure repeated. (With sample weights over 20 g a final wash with 10 ml methylated spirit was found necessary to enable the remainder of the acid to be recovered.) 10 ml each of sodium acetate, hydroxylamine hydrochloride solutions were added to the combined extracts and the funnel well shaken. The remainder of the method followed that given for the calibration.

As completely copper-free reagents were unobtainable a blank determination omitting the copper naphthenate from the oil sample was carried out.

The results obtained using this method are given in Table I.

TABLE I

RESULTS

Wt. of oil taken g	Copper added μg	Spekker drum	Copper found μg ($\pm$ 2 μg)
4.58	48.5	0.59	49
5.23	57	0.52	58.5
10	—	0.95	—
10	11.5	0.86	12
10	53.8	0.55	54
10	93	0.25	95
50	—	0.94	—
52.6	27.2	0.74	27
47.9	84	0.31	85
82.5	26	0.74	27
81.2	12.7	0.84	13
100	—	0.92	—
100.9	9.05	0.85	9.5
100	6.23	0.87	6.5

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It can be seen that the method yields satisfactory results on oil samples weighing from 10-100 g. The figure for the blank varies but little with the quantity of oil taken. The ability shown by the method to work well with large sample weights and its undoubted speed and simplicity, yet yielding results of satisfactory accuracy, are great points in its favour.

ACKNOWLEDGEMENTS

The author wishes to thank his colleague Mr. R. H. A. CRAWLEY for helpful discussions and Mr. L. J. DAVIES, Director of Research, for permission to publish this paper.

SUMMARY

A rapid method for the determination of small amounts of copper in mineral oils is described which avoids the difficult ignition of the organic matter. The copper is extracted with alcoholic hydrochloric acid and determined colorimetrically by extraction of the 2;2-diquinolyl complex with chloroform.

The method operates satisfactorily with sample weights of 10 to 100 g and copper contents of 100 μg to 10 μg.

RÉSUMÉ

Une méthode rapide est décrite pour le dosage du cuivre en faibles teneurs, dans les huiles minérales; elle permet d'éviter les difficiles calcinations de la substance organique. Le cuivre est extrait par l'acide chlorhydrique, en solution alcoolique et dosé colorimétriquement par extraction de son complexe avec le 2;2-diquinolyl, dans le chloroforme. Cette méthode donne de bons résultats pour des échantillons de 10 à 100 g et pour des teneurs en cuivre de 100 μg à 10 μg.

ZUSAMMENFASSUNG

Es wird eine rasche Methode beschrieben um kleine Mengen von Kupfer in Mineralölen zu bestimmen. Sie erlaubt es, die schwierigen Kalzinationen der organischen Substanz zu umgehen. Das Kupfer wird mit Salzsäure in alkoholischer Lösung ausgezogen und kolorimetrisch bestimmt durch Extraktion seines Komplexes mit 2;2' Dichinolyl in Chloroform. Diese Methode gibt gute Resultate für Einwagen von 10 bis 100 g und für Kupfergehalte von 100 μg bis 10 μg.

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MERCURY CELL FOR CATHODIC SEPARATION OF ELEMENTS

by

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The renewal of the surface of the mercury cathode during the deposition of elements represents an important problem, especially when working with elements having a strong negative deposition potential on mercury, since hydrogen overvoltage is appreciably diminished on the unclean surface of the mercury. Good results were not always obtained by the various measures taken for the renewal of the cathode surface, such as stirring of the mercury, its repeated replacement *etc.* CORIOU and coll.[1] renewed the mercury surface by a continual addition of pure mercury from the capillary in an electrolytic cell; through an arrangement the excess of mercury flowed out of the cell. In this manner they succeeded in separating also manganese from the solution after many hours of electrolysis by a very great current density of 4 A/cm^2. This report deals with a method based on the change of the surface tension of mercury with that of the potential difference on the interface mercury-electrolyte. This phenomenon has already been used for industrial purposes in the construction of a cell for electrolytic production of chlorine and alkali-disk-cell[2].

LÉVÊQUE[3] used as a new type of electrode for polarography an amalgamated platinum wire along which mercury flowed. By testing various metals to be used as a wire material[4] we found that Pt, Ni, Fe could be coated with a homogenous layer of mercury if the cathode potential of the wire was sufficiently negative. It was supposed that such an electrode could be used successfully for electrolytic deposition of elements on cathode in general, in which case it would have an advantage over other mercury cathodes because of the continuous and complete renewal of the mercury surface.

In order to confirm this supposition a convenient cell was constructed with which the preliminary experiments were made.

Description of the cell

The cell consists of a glass vessel(a), cathode(b) and anode(c).

The vessel is double-walled having an inner diameter of 18 mm and a height of 120 mm. At the bottom is a stopcock (d) which serves as an outlet for the solution, and a capillary tube (e) for the separation of mercury, having an inner diameter of 2.5 mm. This tube is so formed that the mercury level is about 3 mm below the bottom of the vessel whenever the latter contains 20 ml of electrolyte.

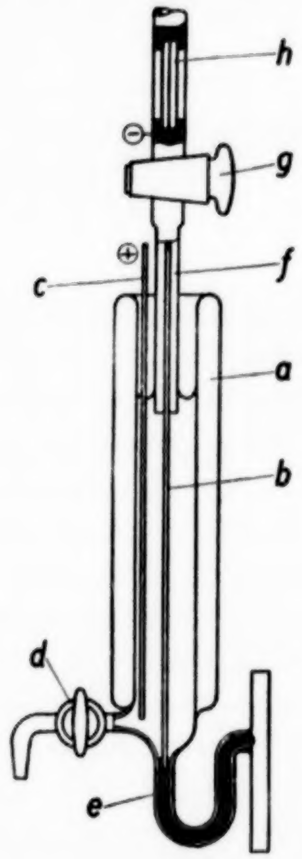

Fig. 1. A mercury wire cathode-cell for electrolytic deposition of elements
a. Cell vessel
b. Nickel wire
c. Platinum foil anode
d. Stopcock for the outlet of the mercury
e. Capillary tube for the separation of mercury
f. Capillary tube
g. Stopcock for the inlet of mercury
h. Capillary tube

The cathode itself consists of a nickel wire having a diameter of 1 mm and a length of 125 mm. One end of the wire is dipped in the mercury in the capillary on the bottom of the vessel, the other end is placed in a capillary (f) whose diameter is 1.2 mm and which is prolonged to the stopcock (g). It is desirable that the part of the wire in the capillary (f) be coated electrolytically with a layer of mercury[4] and that it be drawn into the capillary which has previously been filled with mercury. Thus the electrolyte is prevented from penetrating into the capillary. The part of the wire which is in the electrolyte has a length of 80 mm so that the active surface of the electrode is 2.5 cm^2. A narrow capillary (h), soldered to the wider part of the stopcock by means of a suitable mixture (5 parts of colophony and 1 part of beeswax), serves to regulate the speed of flow of the mercury by adjusting its level above the capillary. Due to the considerable resistance in the capillary (h) the electric contact with mercury must be laid under it.

The anode (c) is made of platinum foil and has a width of 1 mm. It lies parallel to the cathode and at a distance of 8 mm from it and reaches to the bottom of the vessel.

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This cell is manipulated as follows: after the cathode and the anode have been placed into the cell in vertical position, the capillary (e) is filled with mercury by opening the stopcock (g). Then 20 ml of solution to be subjected to electrolysis are poured into the cell and the reopening of the stopcock completes the current circuit. The wire becomes covered with a mercury coating which then flows continuously along it during the whole experiment. The experiment is concluded by allowing the solution to pass through the stopcock (d), the cell is then washed with water and the stopcock closed.

For comparison the known MELAVEN-cell[5], modified by FURMAN AND BRICKER[6], was used. Working conditions are given in Table I.

TABLE I

Type of cell	Cathode surface (cm^2)	Quantity of electrolyte (ml/cm^2)	Cathodic current density (A/cm^2)	Electrode distance (cm)	Quantity of mercury
Melaven-cell	15.20	8	0.24	2.0	400 g
Wire cathode-cell	2.51	8	0.24	0.8	3 g/min

TABLE II

MELAVEN-CELL

Constitution of the electrolyte 10^{-4} g/ml Cu, Cd, Ni and Zn in $1N$ H_2SO_4

Time of electrolysis (hours)	Cu (g/ml)	Cd (g/ml)	Ni (g/ml)	Zn (g/ml)
0.5	under 10^{-7}	$1 \cdot 10^{-5}$	$9.4 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$
1.0	,,	$3.3 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$
1.5	,,	$1.7 \cdot 10^{-6}$	$6.6 \cdot 10^{-6}$	$9.5 \cdot 10^{-7}$
2.0	,,	$1.3 \cdot 10^{-6}$	$1.0 \cdot 10^{-7}$	$9.5 \cdot 10^{-7}$
2.5	,,	under 10^{-7}	*ca.* 5.10^{-8}	*ca.* $2 \cdot 10^{-7}$
3.0	,,	,,	,,	,,

TABLE III

WIRE CATHODE-CELL

Constitution of the electrolyte 10^{-4} g/ml Cu, Cd, Ni and Zn in $1N$ H_2SO_4

Time of the electrolysis (hours)	Cu (g/ml)	Cd (g/ml)	Ni (g/ml)	Zn (g/ml)
0.5	$2.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$
1.0	$2.5 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$
1.5	$1.0 \cdot 10^{-7}$	$2.5 \cdot 10^{-7}$	$1.5 \cdot 10^{-6}$	$5.0 \cdot 10^{-7}$
2.0	under 10^{-7}	under 10^{-7}	$2.0 \cdot 10^{-6}$	$6.0 \cdot 10^{-7}$
2.5	,,	,,	$2.0 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$
3.0	,,	,,	$1.0 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$

EXPERIMENTAL RESULTS

As seen in Tables II and III, by working under normal conditions and by an initial concentration of 10^{-4} g/ml there is no difference in the efficiency of the separation of a mixture containing cations Cu, Cd, Ni and Zn. This also holds for the concentration of 10^{-3} g/ml (Table IV).

TABLE IV

Constitution of the electrolyte 10^{-3} g/ml Cu, Cd, Ni and Zn in $1N$ H_2SO_4
Time of the electrolysis 3 hours

Cell type	Cu (g/ml)	Cd (g/ml)	Ni (g/ml)	Zn (g/ml)
MELAVEN-cell	under 10^{-7}	$3.2 \cdot 10^{-6}$	$2.7 \cdot 10^{-7}$	$3.7 \cdot 10^{-6}$
Wire cathode-cell	,,	under 10^{-7}	$2.7 \cdot 10^{-6}$	$8.5 \cdot 10^{-7}$

However, in the case of manganese (Table V) this new cell shows a well-marked advantage with regard to efficiency of separation.

TABLE V

Constitution of the electrolyte 10^{-4} g/ml manganese in $1N$ H_2SO_4

Cell type	Remained Mn (g/ml)	Time of the electrolysis (hours)
MELAVEN-cell	5.10^{-5}	6
Wire cathode-cell	$1-2 \cdot 10^{-7}$	3

The electrolysis of a solution containing $5 \cdot 10^{-4}$ g/ml of manganese in $1N$ H_2SO_4 was carried out. The current density was 0.8 A/cm². After 45 min of electrolysis no manganese could be detected colorimetrically, neither when in presence of aluminium sulfate (15 g/l) after one hour of electrolysis.

The examination of the various conditions which might have an influence on the working of the cell, *i.e.* the density of the current, speed of the mercury flow, distance from the electrodes, concentration and constitution of the electrolyte *etc.*, are now in the course of study.

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SUMMARY

For the purpose of a cathodic deposition of elements a cell with a wire cathode, along which mercury flows due to sufficient negative potential, was constructed and preliminary tests were made.

In comparing this cell with the modified MELAVEN cell, one can see that the former, in the range of the tested concentrations, is equally as efficient in separating the elements which are usually deposited on the mercury cathode. In the case of manganese this cell has a marked advantage over those used up to now, including that of CORIOU and coll., since it is able to separate manganese quantitatively in a short time from the sulfate solutions used.

With this type of cell it is possible to work with a volume of electrolyte of a few ml and less.

The construction and handling of the cell are simple.

RÉSUMÉ

Afin d'étudier le dépôt cathodique des éléments, l'auteur a construit et examiné une cuve à fil cathodique le long duquel s'écoule du mercure, à un potentiel suffisamment négatif. En comparant avec une cuve du type MELAVEN modifiée, il a été démontré que la cuve en question permet, dans les concentrations essayées, une séparation aussi efficace que celle obtenue habituellement sur la cathode de mercure. Dans le cas du manganèse, cette cuve présente de grands avantages sur les autres modèles (y compris la cuve de CORIOU et coll.); elle permet de séparer quantitativement et très rapidement le manganèse en solution sulfurique. Au moyen de cette cuve, on peut utiliser un volume d'électrolyte de quelques ml et moins. Sa construction et son maniement sont simples.

ZUSAMMENFASSUNG

Zum Zwecke der kathodischen Abscheidung der Elemente wurde eine Zelle mit Drahtkathode, an der infolge eines genügend negativen Potentials Quecksilber entlang fliesst, konstruiert und geprüft.

Beim Vergleich mit der modifizierten Zelle nach MELAVEN wurde festgestellt, dass diese Zelle hinsichtlich der Abscheidungsfähigkeit derjenigen Elemente, die gewöhnlich elektrolytisch an der Quecksilberkathode abgeschieden werden, im Bereich der geprüften Konzentrationen, der genannten in keiner Weise nachsteht. Im Falle von Mangan hat die beschriebene Zelle sogar ausgesprochene Vorzüge gegenüber den bisherigen Zellentypen, einschliesslich der Zelle nach CORIOU und Mitarbeitern, da in ihr das Mangan aus Sulfatlösungen, mit welchen gearbeitet wurde, schnell und vollständig abgeschieden werden kann.

Dieser Zellentypus ermöglicht das Arbeiten mit Elektrolytmengen von einigen ml oder noch weniger.

Die Konstruktion und die Handhabung der Zelle sind einfach.

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SÉPARATION DE TRACES DE MANGANÈSE PAR ÉLECTROLYSE SUR CATHODE DE MERCURE RENOUVELÉE

par

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Une électrolyse sur cathode de mercure renouvelée[1] permet de réaliser un grand nombre de séparations quantitatives, l'une des plus intéressantes étant celle de traces de manganèse. En raison de son potentiel de décharge et compte tenu de sa facilité à s'oxyder à l'anode, l'ion Mn^{+2} apparaît comme particulièrement difficile à réduire sur la cathode à l'état d'élément. Différents auteurs se sont déjà préoccupés du dépôt de manganèse par électrolyse, parmi les plus récentes publications MAXWELL ET GRAHAM[2] dans une bibliographie très complète des différents travaux sur les cathodes de mercure signalent le manganèse comme incomplètement déposé sur cathode de mercure, tout en indiquant différents milieux utilisés en vue d'un dépôt quantitatif[3,4,5,6], LUNDELL ET HOFFMAN[7], BOCK ET HACKSTEIN[8] obtiennent également un dépôt incomplet. McDUFFIE ET HAZLEGROVE[9] dans des solutions de sulfate, sulfite-sulfate, oxalate-sulfate, ont réalisé un dépôt quantitatif du manganèse en utilisant comme anode un fil de platine de faible surface, le pH le plus favorable au dépôt se situant à 2.75.

Nous nous sommes proposés pour notre part d'appliquer la cellule à cathode de mercure renouvelée au dépôt de traces de manganèse (ordre de 1 mg pour 100 ml), en milieu sulfurique ou perchlorique. Nous avons opéré à des pH $\leqslant 1$; nous mettons en évidence l'influence particulièrement importante de l'acidité et de la surface anodique sur la cinétique de dépôt et tentons une interprétation théorique des courbes de cinétique. Nous appliquons la méthode à l'extraction totale de traces de manganèse contenues dans une solution de sulfate de béryllium, perchlorate de calcium, sulfate uraneux.

Appareillage

La cellule à électrolyse est représentée par la Fig. 1. Du mercure gouttant par un capillaire renouvelle continuellement la cathode de mercure de surface 1 cm^2, l'amalgame formé est recueilli dans le bécher (b). Nous avons utilisé pour notre étude du manganèse activé à la pile P_1. A des intervalles de temps de 15 ou 30 minutes, l'activité de 10 ml de la solution est comparée à celle de 10 ml d'une solution témoin, la déperdition d'activité nous donne la quantité de manganèse

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déposé; le contrôle de l'activité de l'anode nous permet de vérifier également la nature du dépôt.

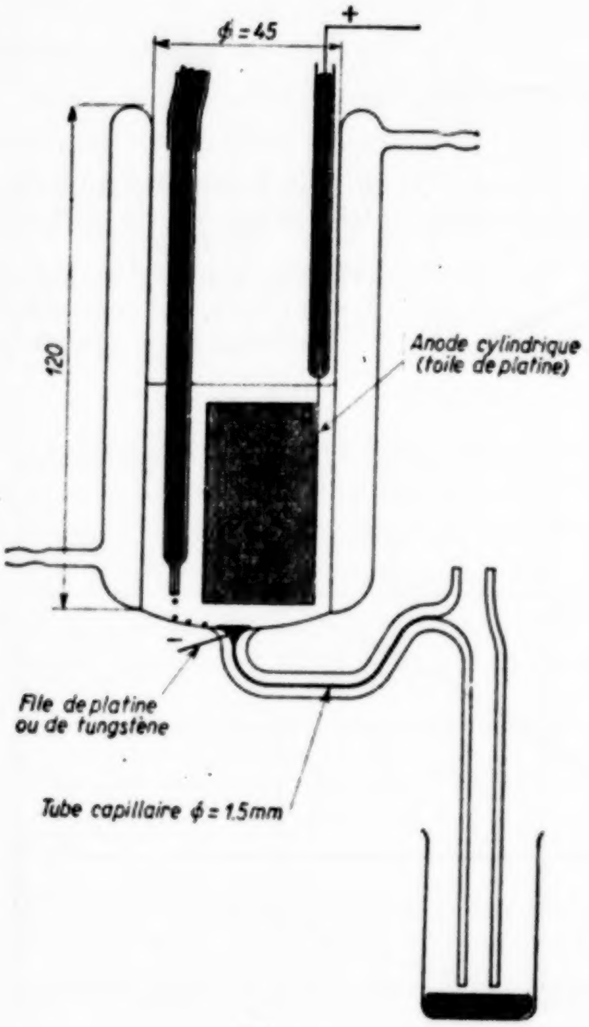
ϕ = 45
+
120
Anode cylindrique (toile de platine)
File de platine ou de tungstène
Tube capillaire ϕ = 1.5mm

Fig. 1.

RÉSULTATS EXPÉRIMENTAUX

Courbe de dépôt

A 100 ml d'une solution d'acide sulfurique 2.5N, on ajoute 400 microgrammes de manganèse. Nous maintenons l'intensité à 4 ampères, la vitesse de renouvellement à 7 ml de mercure par heure, la température à 21° ± 2. L'anode est une électrode de l'appareil de "Bertiaux" constituée par un cylindre en toile de platine perforée et répondant aux caractéristiques suivantes:

hauteur: 50 mm
diamètre: 30 mm
surface totale: 95 cm² environ.

Nous définirons le taux d'extraction τ du manganèse par la relation:

$$\tau = 1 - \frac{\gamma_{(t)}}{\gamma_{(0)}}$$

$\gamma_{(t)}$ et $\gamma_{(0)}$ représentant respectivement la concentration du manganèse en solution à l'instant t et au $t = 0$. Les variations de log $(1—\tau)$ en fonction du temps sont représentées par une droite passant par l'origine (Fig. 2), conséquemment τ doit être de la forme $\tau = 1—e^{-Kt}$ où K est une constante. Nous obtenons dans les conditions précédemment décrites un dépôt cathodique et quantitatif à 1% près, au bout de 7 heures d'électrolyse.

Influence de différents facteurs sur la cinétique du dépôt

La cinétique de dépôt est fonction de la vitesse de renouvellement de la cathode cependant pour une concentration donnée, à partir d'une vitesse suffisante du renouvellement, la cinétique ne dépend plus de cette dernière, le mercure cathodique pouvant être considéré comme non pollué (Fig. 12). Dans l'étude qui va suivre nous nous placerons évidemment dans ces conditions, et caractériserons la cinétique par la valeur du coefficient K, dans les cas où τ obéit à l'équation $1 = 1—e^{-Kt}$.

Concentration initiale

Dans les limites que nous avons étudiées pour $\gamma_{(0)}$ (0.4 microgramme à 12

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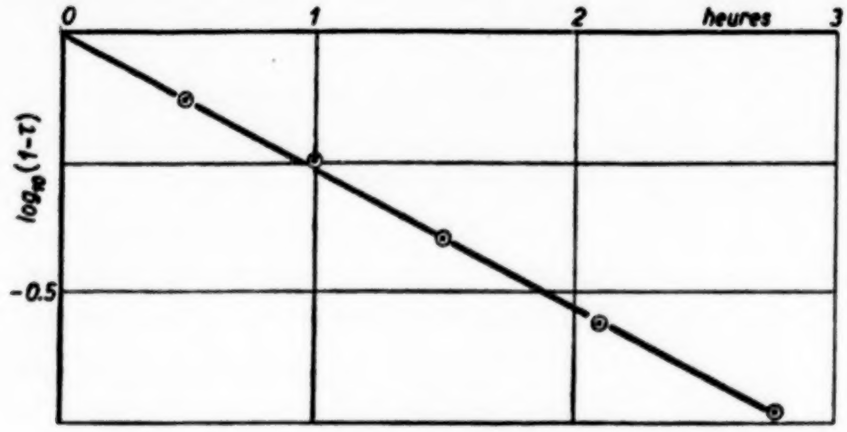

Fig. 2. Transformée logarithmique de la courbe de dépôt. (H_2SO_4 2.5N, $J = 4A$, $t = 21° \pm 2$, $S_a = 95$ cm^2, $V = 100$ ml, $\gamma_{(0)} = 4\mu g/ml$).

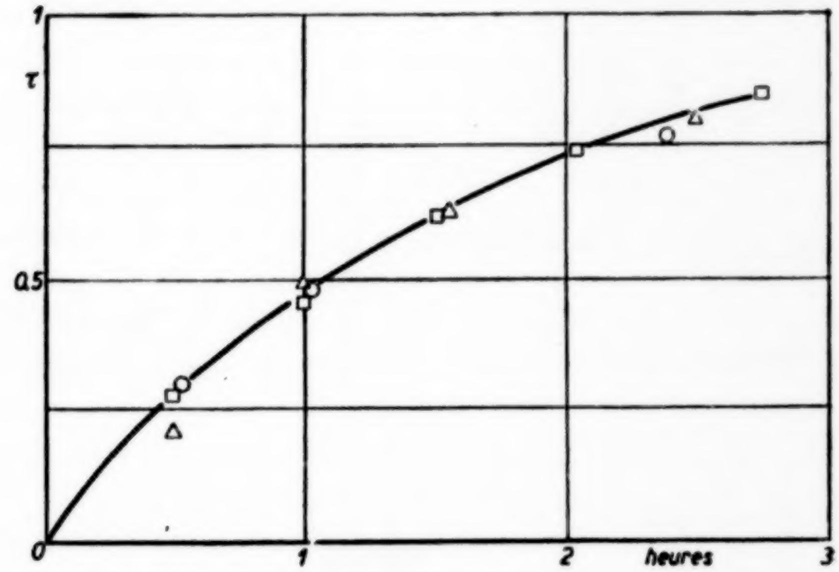

Fig. 3. Influence de la concentration initiale (H_2SO_4 2.5N, $J = 4A$, $t = 21° \pm 2$, $S_a = 95$ cm^2, $V = 100$ ml).

△ $\gamma_{(0)} = 0.4\mu g/ml$
□ $\gamma_{(0)} = 4\mu g/ml$
○ $\gamma_{(0)} = 12\mu g/ml$

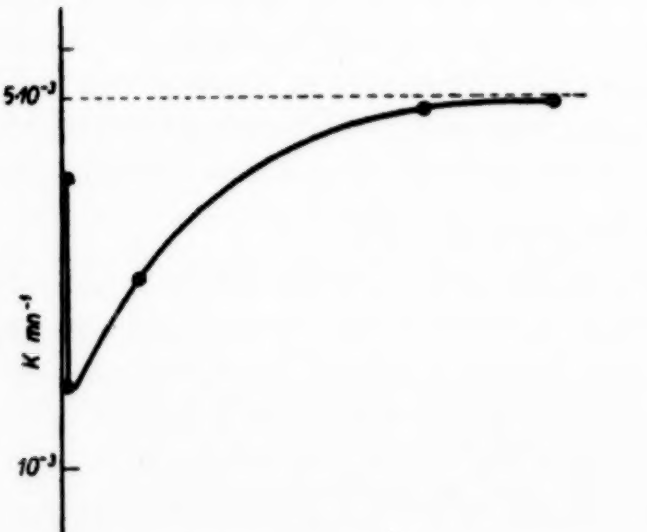

Fig. 4. Influence de la surface anodique. (H_2SO_4 2.5N, $J = 4A$, $t = 21° \pm 2$, $V = 100$ ml, $\gamma_{(0)} = 4\mu g/ml$).

microgrammes/ml), τ est indépendant de la concentration initiale du manganèse en solution (Fig. 3).

Surface anodique

Nous avons utilisé des anodes en platine poli ayant la forme de plaques de surfaces respectives: 0.5 cm², 1 cm², 5 cm², 15 cm², pour les surfaces plus importantes nous nous sommes servis de l'électrode de Bertiaux précédemment décrite ou d'une électrode Kling Lassieur constituée par un panier en toile de platine dont les caractéristiques essentielles sont les suivantes:

hauteur: 50 mm
diamètre: 30 mm
surface totale: 70 cm² environ.

Les résultats obtenus sont représentés sur la Fig. 4. Il est impossible d'opérer avec une électrode de surface inférieure à 0.5 cm², en effet au-dessous de cette valeur on observe l'apparition de MnO_2 en suspension dans la solution.

Sur la Fig. 5 nous remarquons que pour une viscosité constante $(1-\tau)$ s'écarte d'autant plus de la forme exponentielle que la surface anodique est plus faible, compte tenu des limites de concentrations étudiées.

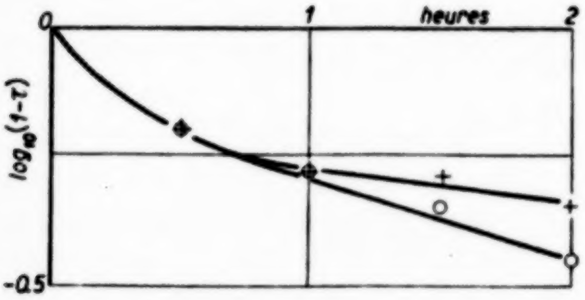

Fig. 5. H_2SO_4 2.5N, $J = 4A$, $t = 30° \pm 2$, $V = 100$ ml, 5% glycérine. ○ surface anodique: 3.5 cm² + surface anodique: 95 cm²

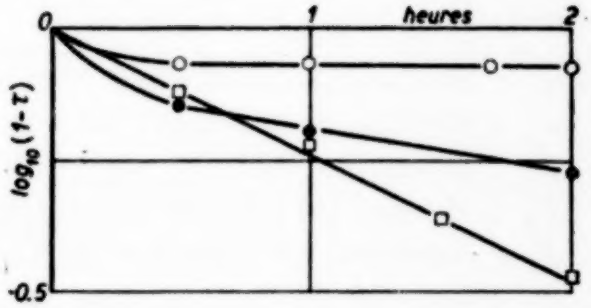

Fig. 6. Influence de la viscosité. (H_2SO_4 2.5N, $J = 4A$, $t = 40° \pm 2$, $S_a = 95$ cm², $V = 100$ ml, $\gamma_{(0)} = 4\mu g/ml$.), ○ 30% glycérine ● 10% glycérine, □ 0% glycérine

Viscosité

Si l'on ajoute de la glycérine afin d'augmenter la viscosité du milieu, les variations $\log_{10}(1-\tau)$ en fonction du temps ne sont plus représentées par une droite passant par l'origine, τ ne répond plus à la formule $\tau = 1-e^{-Kt}$ (Fig. 6).

Intensité

La vitesse de dépôt croît avec l'intensité. Entre 0.5 et 5 Ampères, les variations du coefficient K en fonction de l'intensité peuvent être sensiblement représentées par une fonction linéaire passant par l'origine (Fig. 7).

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INTERPRÉTATION THÉORIQUE DES COURBES DE DÉPÔT

Considérons à la cathode la décharge d'un cation M, s'il s'agit d'une réaction "irréversible", les variations $i = \mathrm{f}\,(E_c)$[10] de la densité de courant en fonction du potentiel cathodique E_c peuvent s'écrire:

$$i = -kn_T\,Fa_e\,\mathrm{e}^{-\frac{anF}{RT}E_c}$$

le bilan se traduisant par l'équation:

$$\frac{i}{n_T F} + \frac{tI_c}{ZF} + k_d\,[a - a_e] = 0$$

Avec les notations suivantes:

k : constante dépendant en particulier du choix de l'origine des potentiels et de l'énergie d'activation.
n_T: nombre total d'électrons mis en jeu à l'électrode dans la réaction électrochimique.
a_e : activité de l'ion M dans la solution au voisinage de l'électrode.
n : nombre d'électrons mis en jeu à l'électrode dans la réaction intermédiaire la plus lente se produisant au cours du "dépôt cathodique".
a : coefficient de transfert relatif au "dépôt cathodique".
t : nombre de transport du corps électrolysé.
Z : sa charge comptée algébriquement.
I_c : densité de courant cathodique totale.
k_d : constante de diffusion de l'ion M dans la solution.
a : activité de l'ion M dans la solution.

Nous conservons à F, R, T, leur signification habituelle.

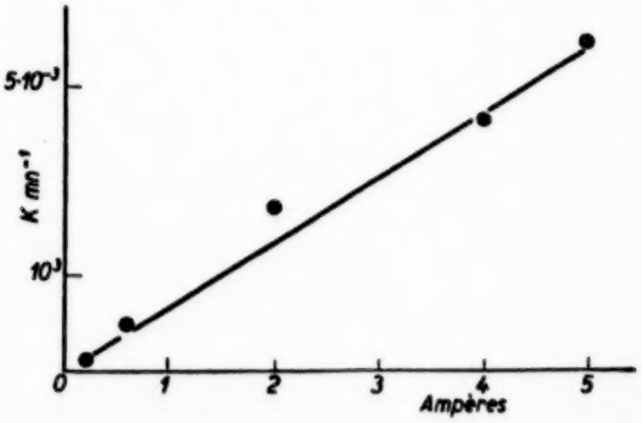

Fig. 7. Influence de l'intensité.
(H_2SO_4 2.5*N*, $t = 21° \pm 2$, $S_a = 95$ cm², $V = 100$ ml, $\gamma_{(0)} = 4\mu$g/ml)

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Par convention nous donnons une valeur négative à la densité de courant relative à une "réduction cathodique" et une valeur positive à la densité relative à une "oxydation anodique".

Nous déposons M à la cathode en dégageant de fortes quantités d'hydrogène. Si M est à l'état de traces dans un milieu d'acide sulfurique ou perchlorique dont la normalité est $\geqslant 1$, les concentrations de tous les ions en solution exceptée celle de M restent pratiquement constantes au cours de l'électrolyse, d'après la définition même du nombre de transport t du corps M, t est sensiblement proportionnel à la concentration, donc à l'activité a de l'ion M dans la solution; nous pouvons en conséquence poser $t = \lambda a$, λ représentant une constante de proportionnalité.

La combinaison des équations initiales permet d'écrire:

$$i = -kn_T F \, e^{-\frac{\alpha n F}{RT} E_c} \left[\left(\frac{\lambda I_c}{k_d Z F} + 1 \right) a + \frac{i}{k_d n_T F} \right]$$

Enfin la densité i_d du courant de diffusion est donnée par:

$i_d = - n_T k_d \, F a$ et la densité de courant limite par $i_l = -n_T \left[k_d F + \frac{\lambda I_c}{Z} \right] a$

S'il s'agit d'une oxydation anodique les formules sont identiques à celles que nous venons d'établir à condition de remplacer le coefficient α, par le coefficient de transfert β relatif à une oxydation anodique et le potentiel $-E_c$ par le potentiel E_a.

Soit en milieu acide un ion Mn^{+2} susceptible de se décharger à la cathode ou de s'oxyder en MnO_4^- à l'anode, dans un but de simplification nous admettrons comme possibles les seules réactions suivantes:

Cathode: (1) $Mn^{+2} + 2\,e \rightarrow Mn$.
(2) $MnO_4^- + 8\,H^+ + 5\,e \rightarrow Mn^{+2} + 4\,H_2O$.
(3) $H^+ + e \rightarrow \frac{1}{2}H_2$.
Anode: (4) $Mn^{+2} - 5\,e + 4\,H_2O \rightarrow MnO_4^- + 8\,H^+$.
(5) $OH^- - e \rightarrow \frac{1}{4}O_2 + \frac{1}{2}H_2O$.

La Fig. 8 représente la disposition présumée des courbes de polarisation se rapportant à ces différentes réactions; les indices correspondant aux numéros d'ordre des différentes réactions:

$$i_1 = - k_1 n_{T,1} F \, e^{\frac{-\alpha_1 n_1 F}{RT} E_c} \left[\left(\frac{\lambda_1 I_c}{k_{d,1} Z_1 F} + 1 \right) a_1 + \frac{i_1}{k_{d,1} n_{T,1} F} \right] \quad (1')$$

$$i_2 = - n_{T,2} \left[k_{d,2} F - \frac{\lambda_2 I_c}{Z_2} \right] a_2 \quad (2')$$

$$i_3 = - k_3 F a_3 \, e^{-\frac{\alpha_3 F}{RT} E_c} \quad (3')$$

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$$i_4 = k_4 n_{T,2}\, F\, e^{\frac{\beta_4 n_4 F}{RT} E_a} \left[\left(\frac{-\lambda_1 I_a}{k_{d,1} Z_1 F} + 1 \right) a_1 - \frac{i_4}{k_{d,1} n_{1'2} F} \right] \qquad (4')$$

$$i_5 = k_5 F a_5\, e^{\frac{\beta_5 F}{RT} E_a} \qquad (5')$$

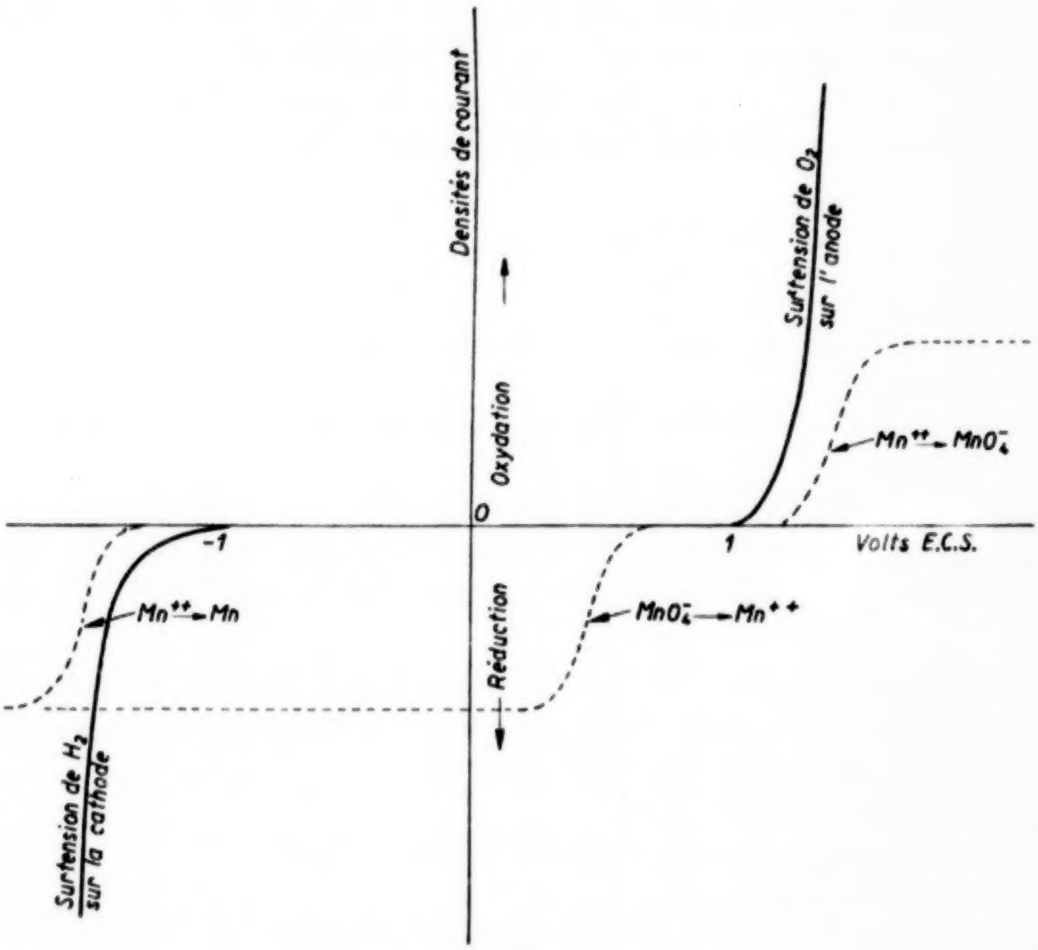

Fig. 8.

Eliminons E_c entre les équations (1′) et (3′):

$$i_1 = \frac{-n_{T,1} F \left[\frac{\lambda_1 I_c}{k_{d,1} Z_1 F} + 1 \right] a_1}{\frac{1}{k_{d.1}} + \frac{1}{k_1} \left[- \frac{k_3 F a_3}{i_3} \right] \frac{a_1 n_1}{a_3}}$$

L'intensité J traversant la cellule étant de plusieurs ampères et la quantité initiale de manganèse en solution de l'ordre de $0.5 \cdot 10^{-3}$ g, nous pouvons assimiler

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i_3 à $\frac{J}{S_c}$, S_c représentant la surface cathodique. L'intensité I_1 due à la réaction $Mn^{+2} + 2\,e \rightarrow Mn$ peut en conséquence s'exprimer par la formule:

$$I_1 = \frac{-\,n_{T,1}\,FS_c\left[\frac{\lambda_1 J}{k_{d,1}Z_1FS_c} + 1\right]a_1}{\frac{1}{k_{d,1}} + \frac{1}{k_1}\left[-\frac{k_3\,FS_ca_3}{J}\right]^{\frac{a_1n_1}{a_3}}}$$

Nous pouvons mettre I_1 sous la forme $I_1 = -A_1c_1$, c_1 représentant la concentration de Mn^{+2} en solution à un instant donné, A_1 une constante égale à:

$$\frac{n_{T,1}FS_cf_1\left[\frac{\lambda_1 J}{k_{d,1}Z_1FS_c} + 1\right]}{\frac{1}{k_1}\left[\frac{k_3FS_ca_3}{J}\right]^{\frac{a_1n_1}{a_3}} + \frac{1}{k_{d,1}}}$$

, f_1 le coefficient d'activité de l'ion Mn^{+2} dans la solution.

Eliminant de même E_a entre les équations (4') et (5'), l'intensité I_4 due à la réaction $Mn^{+2} \rightarrow MnO_4^-$ peut se mettre sous la forme $I_4 = A_4c_1$; l'intensité I_2 peut elle-même s'écrire $I_2 = -A_2c_2$; c_2 représentant la concentration de MnO_4^- dans la solution, les constantes A_4 et A_2 étant définies respectivement par:

$$\frac{n_{T,2}FS_af_1\left[\frac{-\lambda_1 J}{k_{d,1}Z_1FS_a} + 1\right]}{\frac{1}{k_{d,1}} + \frac{1}{k_4}\left[\frac{k_5FS_aa_5}{J}\right]^{\frac{\beta_4n_4}{\beta_5}}} \quad \text{et} \quad n_{T,2}S_cf_2\left[k_{d,2}F - \frac{\lambda_2 J}{Z_2S_c}\right]$$

; S_a représentant la surface anodique, f_2 le coefficient d'activité de l'ion MnO_4^- en solution.

Les cinétiques de réactions sont régies par:

$$-\frac{dc_1}{dt} = \frac{A_1c_1}{n_{T,1}FV} - \frac{A_2c_2}{n_{T,2}FV} + \frac{A_4c_1}{n_{T,2}FV}$$

$$-\frac{dc_2}{dt} = \frac{A_2c_2}{n_{T,2}FV} - \frac{A_4c_1}{n_{T,2}FV}$$

,V désignant le volume de solution.

Posons: $\frac{A_1}{n_{T,1}FV} = A_1'$, $\frac{A_2}{n_{T,2}FV} = A_2'$, $\frac{A_4}{_{T,2}FV} = A_4'$ nous avons:

$$-\frac{dc_1}{dt} = (A_1' + A_4')\,c_1 - A_2'c_2$$

$$-\frac{dc_2}{dt} = A_2'c_2 - A_4'c_1.$$

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Désignons par $\gamma_{(t)}$ la concentration totale dans la solution du manganèse à un instant t,

$$\gamma_{(t)} = c_1 + c_2 \text{ d'où} : -\frac{d\gamma_{(t)}}{dt} = A_1'c_1$$

$$\text{et} \quad -\frac{dc_1}{dt} = (A_1' + A_2' + A_4')\,c_1 - A_2'\gamma_{(t)}$$

En éliminant c_1 entre ces 2 équations:

$$\frac{d_2\gamma_{(t)}}{dt^2} + (A_1' + A_2' + A_4')\,\frac{d\gamma_{(t)}}{dt} + A_1'A_2'\gamma_{(t)} = 0$$

Les racines r_1 et r_2 de l'équation caractéristique sont réelles.

Posons: $r_1 = b_1 + b_2$
$r_2 = b_1 - b_2$

$$\text{avec} \quad b_1 = \frac{-[A_1' + A_2' + A_4']}{2}, \quad b_2 = \frac{\sqrt{(A_1' + A_2' + A_4')^2 - 4\,A_1'A_2'}}{2}$$

d'où l'intégrale générale: $\gamma_{(t)} = Be^{b_1t}ch\,[b_2t + \Phi]$,

B et Φ représentant 2 constantes définies par les conditions initiales: Au temps

$$t = 0, \ \gamma_{(0)} = Bch\Phi \ \text{et} \ \left(\frac{d\gamma_{(t)}}{dt}\right) = B\,[b_2sh\Phi + b_1ch\Phi] = -A'_1\gamma_{(0)}$$

Nous pouvons poser: $\dfrac{\gamma_{(t)}}{\gamma_{(0)}} = 1 - \tau = Ce^{b_1t}ch\,[b_2t + \Phi]$

τ représentant le taux d'extraction du manganèse, C une constante égale à $\dfrac{1}{ch\Phi}$

Nous retrouvons immédiatement un résultat expérimental: *τ ne dépend pas de* $\gamma_{(0)}$

Passant aux logarithmes:

$\log_e (1-\tau) = -\log_e ch\Phi + b_1t + \log_e ch\,(b_2t + \Phi)$;

si $b_2t + \Phi > 2$, $\log_e ch\,(b_2t + \Phi) \sim 1.04\,(b_2t + \Phi) - 0.79$, d'où:

$\log_e (1-\tau) \sim (b_1 + 1.04\,b_2)\,t + 1.04\Phi - \log_e ch\,\Phi - 0.79$.

τ sera de la forme $\tau = 1 - e^{-Kt}$, K représentant une constante, pour $1.04\Phi - \log_e ch\Phi - 0.79 = 0$; cette condition est vérifiée avec une approximation suffisante lorsque $\Phi > 2$ ou $th\,\Phi > 0.964$,

$$\text{c'est à dire} \ \frac{-b_1 - A_1'}{b_2} = \frac{A_2' + A_4' - A_1'}{\sqrt{(A_1' + A_2' + A_4')^2 - 4\,A_1'A_2'}} > 0.964.$$

Dans le cas où $\Phi < 2$, tant que $b_2t + \Phi < 2$ c'est à dire $t < \dfrac{2 - \Phi}{b_2}$, la courbe $\log (1-\tau) = f(t)$ n'est plus une fonction linéaire du temps; elle le redevient pour $t > \dfrac{2 - \Phi}{b_2}$, conformément aux résultats expérimentaux de la Fig. 6.

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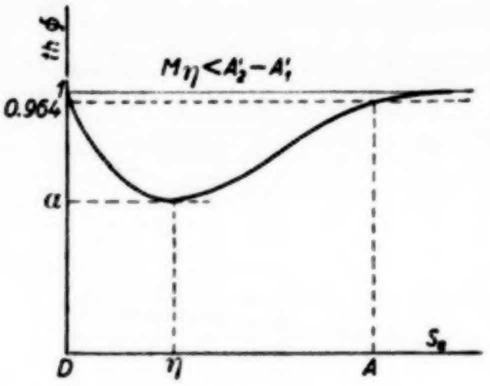

Fig. 9a

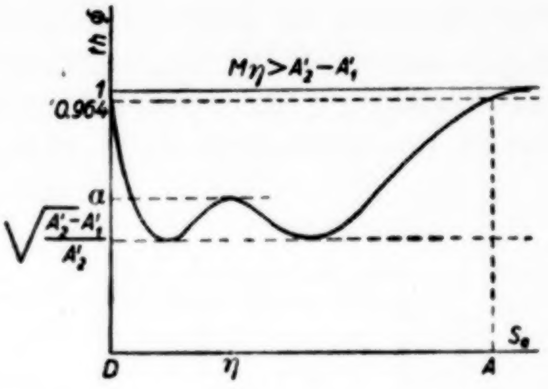

Fig. 9b

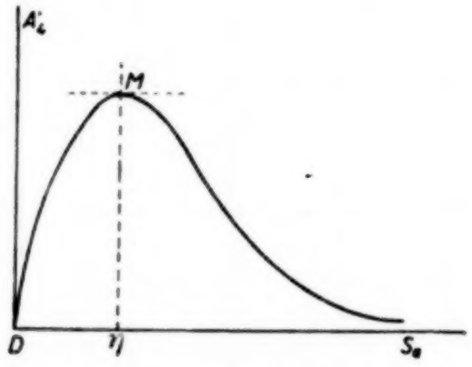

Fig. 9

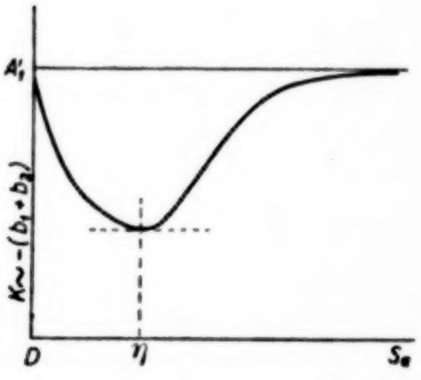

Fig. 10

Influence de la surface anodique

La surface anodique S_a intervient dans le terme A_4' qui peut être mis sous la forme $A_4' = \dfrac{S_a - D}{ES_a \frac{\beta_4 n_4}{\beta_5} + F}$, D, E, F représentant 3 constantes posities. Bien qu'il soit pratiquement impossible de calculer l'expression $\dfrac{\beta_4 n_4}{\beta_5}$ on a toutes raisons de supposer qu'elle est supérieure à 1, s'il en est ainsi les variations de A_4' en fonction de S_a sont représentées par la courbe de la Fig. 9, celles de $th\Phi$ par les courbes des Fig. 9a et 9b suivant que la valeur du maximum de A_4' est inférieure ou supérieure à $A_2' - A_1'$. Nous plaçant par exemple dans le cas de la Fig. 9a, mais en considérant le minimum α de $th\Phi$ inférieur à 0.964 nous pouvons déduire en fonction de S_a la somme $-(b_1 + b_2)$, Fig. 10. Nous retrouvons la forme de courbe expérimentale de la Fig. 4.

APPLICATIONS

Séparation de traces de manganèse.

1. D'une solution de sulfate de béryllium

Les Fig. 11 et 11 bis représentent la vitesse de dépôt de 400 microgrammes de

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manganèse dans 100 ml d'une solution de sulfate de béryllium, 2.5 N en acide sulfurique et contenant 2 g de béryllium ($J = 4\ A$; $t = 42° \pm 2$; $S_a = 70\ cm^2$). Dans les conditions expérimentales τ est de la forme $\tau = 1 - e^{-Kt}$. L'influence de la vitesse de renouvellement de la cathode et celle de l'acidité sont mises en

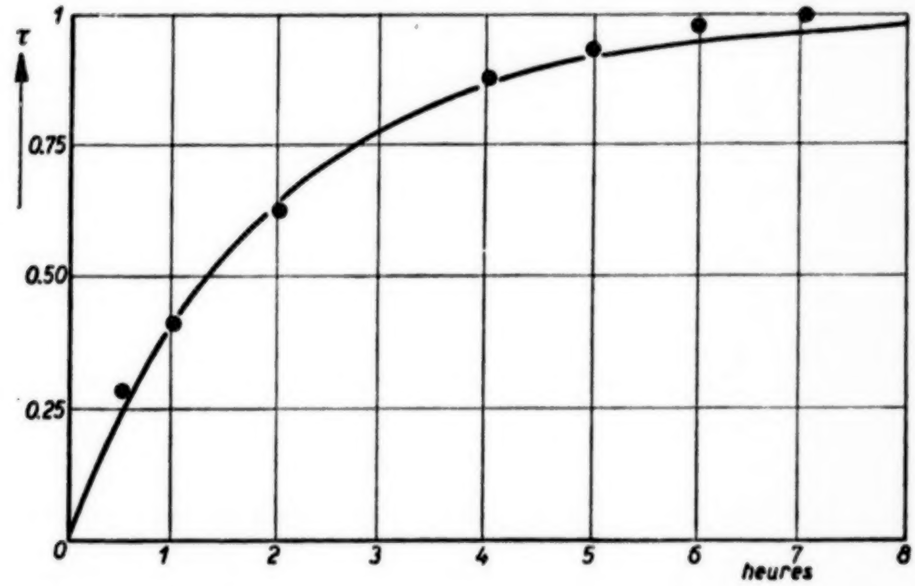

Fig. 11. Courbe de dépôt dans une solution de $BeSO_4$.
(H_2SO_4 2.5N, $J = 4A$, $t = 42° \pm 2$, $S_a = 70\ cm^2$, $V = 100$ ml, $\gamma_{(0)} = 4 \mu g/ml$) Be = 20 mg/ml)

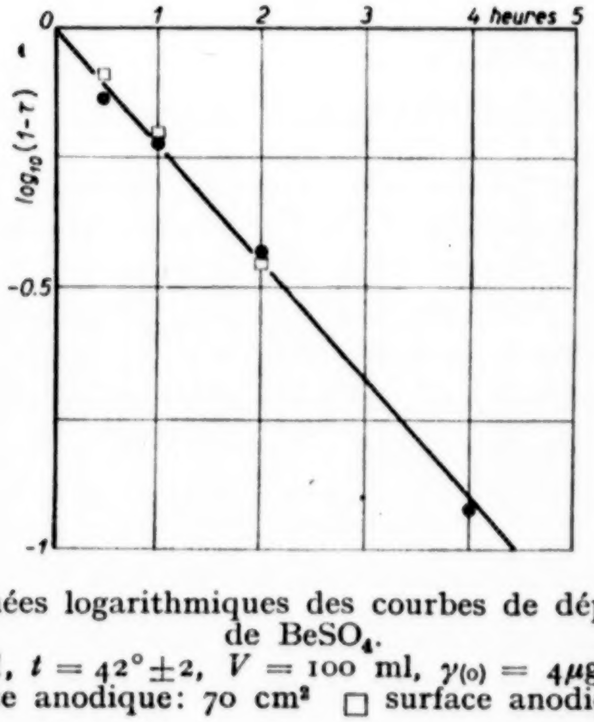

Fig. 11bis. Transformées logarithmiques des courbes de dépôt dans une solution de $BeSO_4$.
(H_2SO_4 2.5N, $J = 4A$, $t = 42° \pm 2$, $V = 100$ ml, $\gamma_{(0)} = 4 \mu g/ml$, Be = 20 mg/ml)
● Surface anodique: 70 cm² □ surface anodique 95 cm²

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évidence par les Fig. 12 et 13. La brusque variation du coefficient K lorsque l'acidité est inférieure à $2.2N$ semble correspondre à l'apparition de MnO_2 en suspension dans la solution, au-dessous de $1N$ le dépôt de MnO_2 adhère à l'anode.

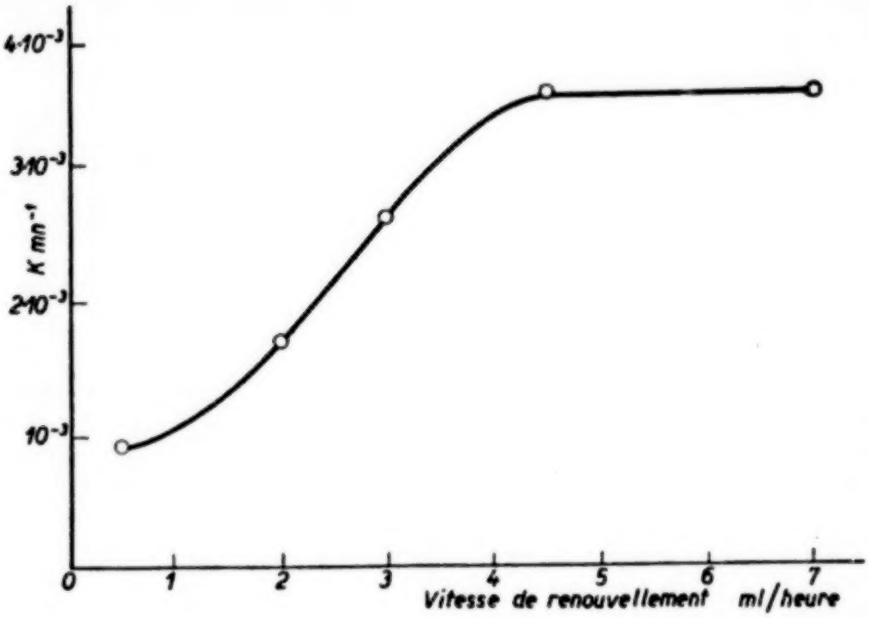

Fig. 12. Influence du renouvellement cathodique sur la cinétique de dépôt dans une solution de $BeSO_4$.
(H_2SO_4 $2.5N$, $J = 4A$, $t = 42° \pm 2$, $S_a = 70$ cm², $V = 100$ ml, $\gamma_{(0)} = 4\mu$g/ml, Be = 20 mg/ml)

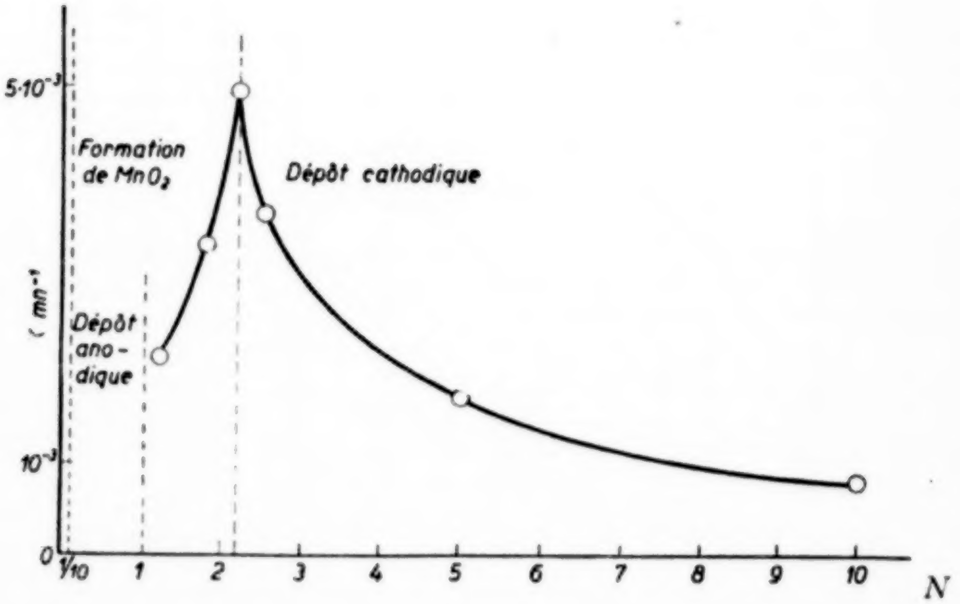

Fig. 13. Influence de l'acidité sur le cinétique de dépôt dans une solution de $BeSO_4$.
($J = 4A$, $t = 42° \pm 2$, $S_a = 70$ cm², V = 100 ml, $\gamma_{(0)} = 4$ μg/ml, Be = 20 mg/ml)

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2. *D'une solution de perchlorate de calcium*

400 microgrammes de manganèse ajoutés à 100 ml d'une solution de perchlorate de calcium 2.5N en acide perchlorique et contenant 5 g de calcium s'extraient suivant la courbe de la Fig. 14 ($J = 4A$; $t = 25° \pm 2$; $S_a = 70$ cm²) τ répond à la formule $\tau = 1 - e^{-Kt}$

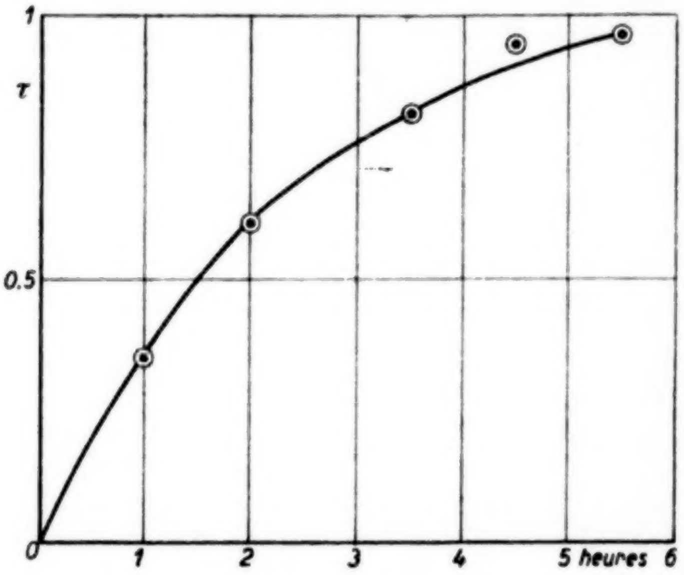

Fig. 14. Courbe de dépôt dans une solution de $Ca(ClO_4)_2$
($J = 4A$, $t = 25° \pm 2$, $S_a = 70$ cm², $V = 100$ ml, $\gamma_{(0)} = 4 \mu g/ml$, Ca = 50 mg/ml)

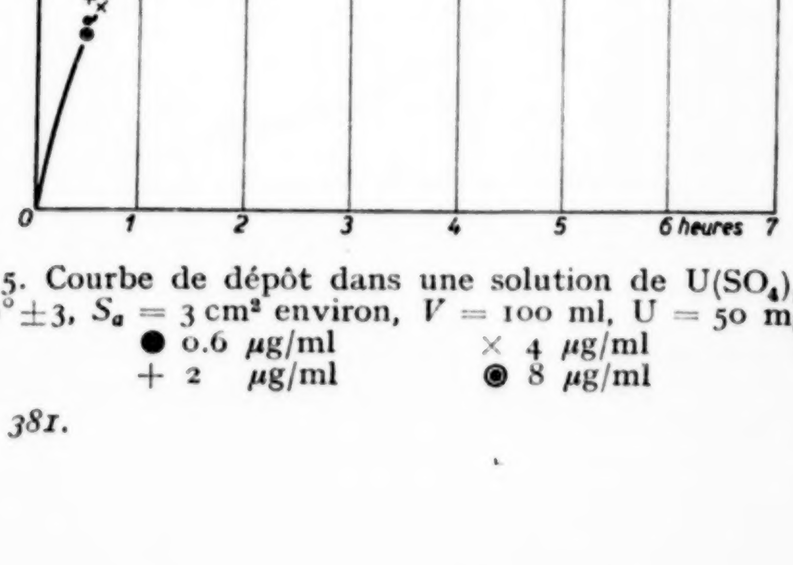

Fig. 15. Courbe de dépôt dans une solution de $U(SO_4)_2$
($J = 3A$, $t = 28° \pm 3$, $S_a = 3$ cm² environ, $V = 100$ ml, U = 50 mg/ml, pH = 0.6)

● 0.6 µg/ml × 4 µg/ml
+ 2 µg/ml ◉ 8 µg/ml

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3. D'une solution de sulfate uraneux

La Fig. 15 montre qu'il est possible de déposer quantitativement à la cathode des traces de manganèse contenues dans 100 ml d'une solution de sulfate uraneux renfermant 5 g d'uranium, à condition d'opérer vers pH = 0.6. Dans les conditions expérimentales τ est bien indépendant de $\gamma_{(0)}$, mais ne répond pas à la formule $\tau = 1 - e^{-Kt}$

REMERCIEMENT

Nous tenons à remercier vivement Monsieur le Professeur CHARLOT qui, au cours de notre travail, a bien voulu nous aider de ses conseils.

RÉSUMÉ

Les conditions d'électrolyse décrites par les auteurs permettent d'obtenir un dépôt quantitatif de traces de manganèse contenues dans des solutions sulfuriques ou perchloriques. Des considérations théoriques basées sur l'application des courbes de polarisation amènent à retrouver un certain nombre de résultats expérimentaux concernant en particulier l'influence de différents facteurs sur la cinétique du dépôt.

SUMMARY

The authors describe conditions of electrolysis which permit a quantitative deposit of traces of manganese to be obtained from sulphate and perchlorate solutions. Theoretical considerations based on the application of polarisation curves lead to a quantitative explanation of some of the experimental results, especially those concerned with the effect of different factors on the kinetics of deposition.

ZUSAMMENFASSUNG

Die von den Autoren beschriebenen elektrolytischen Bedingungen erlauben, einen quantitativen Niederschlag von Mangan-Spuren zu erhalten, welche in schwefel — oder perchlorsauren Lösungen enthalten sind. Theoretische Betrachtungen, basiert auf der Anwendung von Polarisationskurven, führen zur Erklärung einer gewissen Anzahl experimenteller Resultate, welche hauptsächlich den Einfluss betreffen, welchen verschiedene Faktoren auf die Kinetik der Niederschlagsbildung ausüben.

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QUANTITATIVE ELEKTROLYTISCHE ERZEUGUNG VON PERMANGANATIONEN *

von

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Durch primäre anodische Oxydationen und kathodischen Reduktionen, oder durch sekundäre Reaktionen der primär gebildeten Produkte mit den zu bestimmenden Jonen, konnten bis jetzt mit vollem Erfolg mannigfaltige coulometrische Titrationen ausgeführt werden[1-13]. Durch anodisch primär aus Lösungen von Kaliumjodid gebildetes Jod kann, wie wir unlängst gezeigt haben[14], Thiosulfat sehr genau quantitativ bestimmt werden, wodurch die Möglichkeit gegeben wurde eine der wichtigen Titrationen coulometrisch schnell und genau auszuführen und ausserdem die Titereinstellung von Thiosulfatlösungen ohne vorher bereitete Jodlösungen zu bewerkstelligen, und so, im Sinne unseren Vorschlags[15] an die Internationale Union für reine und angewandte Chemie[16], das Coulomb als Grundeinheit, anstelle von Masse, in die gesamte Analytische Chemie einzuführen.

Unser Interesse wurde auch der Möglichkeit gewidmet, die coulometrische Permanganatometrie auszuarbeiten und sämtliche, analytisch wichtigen und interessanten Bestimmungen mit Permanganationen auch coulometrisch zu ermöglichen[17]. Dadurch könnte den coulometrischen Bestimmungen ein neues Arbeitsgebiet eröffnet werden, was den Vorteil bieten würde, dass wir uns von der Bereitung, genauen Einstellung und Erhaltung der Standardlösungen befreien und noch ein Gebiet der Analytischen Chemie der Abmessung durch das Coulomb, als Grundeinheit und Ursubstanz erschliessen könnten. Ausserdem könnten dadurch auch coulometrische Oxydationen durch Permanganat für präparative Zwecke ermöglicht werden, und zwar mit konstantem erwünschten minimalem oder beträchtlichem Überschuss an Permanganat, der von Fall zu Fall bequem zu variieren ist, und zwar mit einer durch den vorhandenen Überschuss regelbaren Geschwindigkeit, was seine besonderen Vorteile haben könnte.

Für die Ermöglichung der coulometrischen Permanganatometrie oder der Oxydationen für präparative Zwecke, sollte zuerst eine der Hauptbedingungen erfüllt werden. Es sollten nämlich zuerst prinzipiell die Möglichkeit der quantitativen, oder wenigstens mit konstantem Nutzeffekt erfolgenden, Erzeugung von Permanganationen gefunden, sowie die entsprechenden Arbeitsbedingungen festgestellt werden. Um diese prinzipielle Möglichkeit zu prüfen, schien uns, nach vorangehenden Vorversuchen und theoretischen Erwägungen, der einzig begründete Weg, die Durchführung eines systematischen Studiums der Potentiale der Arbeitsanoden in wässrigen Lösungen von Mangansulfat und Schwefelsäure verschiedener Konzentrationen und in verschiedenen gegenseitigen Verhältnissen, sowie der Elektrolysenprodukte an der Anode. Die theoretischen Betrachtungen der zu erwartenden Prozesse und Anodenprodukte boten schon vielversprechende Aussichten, dass man auch experimentell die Bedingungen für eine quantitative Erzeugung von Permanganationen wird ausarbeiten können, um sie weiter für quantitative coulometrische permanganatometrische Bestimmungen oder präparative Oxydationen auszuwerten.

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Die elektrolytische Erzeugung von Permanganat in alkalischen Lösungen kam für unsere Zwecke, der coulometrischen Anwendung, nicht in Betracht, da schon das Manganat ein Oxydationsmittel ist[18]. Mit der Frage der elektrolytischen Erzeugung von Permanganat aus Mangansulfat haben sich vor uns DIFFENBACH[19] und vornehmlich CAMBEL[20] befasst. CAMBEL erzeugte Permanganat in schwefelsauren Lösungen von Mangansulfat in Anwesenheit von Kaliumsulfat. Wir konnten experimentell zeigen, dass unter den von ihm angegebenen optimalen Bedingungen das Permanganat nicht quantitativ gebildet wird, hauptsächlich wegen ungenügender Manganionenkonzentration, sondern dass zu gleicher Zeit Sauerstoff neben geringeren Mengen von Mangandioxyd abgeschieden wird. Die Möglichkeit der Anwendung eines so zu benennenden „Grundelektrolyten" in der von CAMBEL angegebenen Zusammensetzung schied daher im voraus aus.

Die theoretische Erörterung der Möglichkeit einer quantitativen Erzeugung von Permanganationen aus sauren Mangansulfatlösungen ergab folgendes. Bei der Elektrolyse von sauren wässrigen Lösungen von Mangansulfat an indifferenten Anoden, können an der Anode als primäre oder sekundäre Produkte Sauerstoff, Mangandioxyd, Permanganat, Persulfat oder Ozon entstehen. Da für die Bildung von Persulfat und Ozon sehr positive Potentiale benötigt werden, die unter den angegebenen Arbeitsbedingungen praktisch nicht erreicht werden, beschränkten wir unsere Betrachtung nur auf die Entstehungsbedingungen von Sauerstoff, Permanganat und Mangandioxyd, um Einsicht in die Möglichkeit der Berechnung der Potentiale und der Reihenfolge der Entstehung der einzelnen in Betracht kommenden Oxydationsprodukte, sowie in den Einfluss der Konzentration von Säure und Mangansulfat und ihres gegenseitigen Verhältnisses zu bekommen.

Im Falle der Sauerstoffabscheidung kommt an der Anode folgende Reaktion in Betracht

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad (I)$$

beziehungsweise eine einfache Wasserzerlegung. Das Anodenpotential für die entsprechende Sauerstoffabscheidung kann aus der folgenden Gleichung berechnet werden

$$e_{O_2} = e_{0O_2} + \frac{RT}{nF} \ln \frac{a_{O_2} \cdot (a_{H^+})^4}{(a_{H_2O})^2} \tag{1}$$

Für das Normalpotential des Sauerstoffs von $e_{0O_2} = +1.23$ V und einen Sauerstoffdruck von 1 Atm ergiebt sich bei 25° für das Abscheidungspotential des Sauerstoffs

$$e_{O_2} = 1.23 - 0.059 \text{ pH} \tag{2}$$

Auch bei der Stromdichte 0 Amp/qcm kann der Sauerstoff bei diesem Mindestpotential, wegen der Überspannung, nicht abgeschieden werden, so dass das Potential noch um den Betrag der Sauerstoffüberspannung η_{O_2} positiver gemacht werden sollte, um zu dem Anodenpotential zu kommen, bei welchem theoretisch die Sauerstoffabscheidung möglich ist

$$e_{O_2} = 1.23 - 0.059 \text{ pH} + \eta_{O_2} \tag{3}$$

Bei der Abscheidung von Mangandioxyd an der Anode spielt sich folgende Reaktion ab

$$Mn^{+2} + 2\,H_2O \rightarrow MnO_2 + 4\,H^+ + 2\,e^- \tag{II}$$

und das Gleichgewichtspotential der Anode ist dabei wie folgt gegeben

$$e_{Mn^{+2}/MnO_2} = e_{0Mn^{+2}/MnO_2} + \frac{RT}{nF} \ln \frac{a_{MnO_2} \cdot (a_{H^+})^4}{a_{Mn^{+2}} \cdot (a_{H_2O})^2} \tag{4}$$

Mit dem Normalpotential für diese Reaktion $e_{0_{Mn^{+2}/MnO_2}} = +1.24$ V bekommt man bei 25°

$$e_{Mn^{+2}/MnO_2} = 1.24 - 0.118 \text{ pH} - 0.0295 \log a_{Mn^{+2}} \tag{5}$$

Im Falle, dass an der Anode Permanganat gebildet wird, spielt sich dabei die Reaktion

$$Mn^{+2} + 4\,H_2O \rightarrow MnO_4^- + 8\,H^+ + 5\,e^- \tag{III}$$

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ab, und das Elektrodenpotential ist durch den Ausdruck

$$e_{\mathrm{Mn}^{+2}/\mathrm{MnO}_4^-} = e_{0\,\mathrm{Mn}^{+2}/\mathrm{MnO}_4^-} + \frac{RT}{nF} \ln \frac{a_{\mathrm{MnO}_4^-} \cdot (a_{\mathrm{H}^+})^8}{a_{\mathrm{Mn}^{+2}} \cdot (a_{\mathrm{H_2O}})^4}$$

gegeben. Nimmt man für das Anodennormalpotential den Wert $e_{0\,\mathrm{Mn}^{+2}/\mathrm{MnO}_4^-} = +\ 1.51$ V, so kommt man zu dem endgültigen Ausdruck für das Potential der Arbeitsanode bei 25°

$$e_{\mathrm{Mn}^{+2}/\mathrm{MnO}_4} = 1.51 + 0.0118 \log a_{\mathrm{MnO}_4^-} - 0.0118 \log a_{\mathrm{Mn}^{+2}} - 0.0944\ \mathrm{pH} \quad (7)$$

Aus den Potentialausdrücken 3, 5 und 7 kommt man zu dem Schluss, dass die Bildung von Sauerstoff, Mangandioxyd und Permanganat vom pH des Elektrolyten abhängig ist. Aus der Gleichung 3 ist ersichtlich, dass eine Änderung des pH um eine Einheit eine Änderung des Anodenpotentials um 59 mV nach sich zieht, und aus der Gleichung 5 kann der Schluss gezogen werden, dass dieselbe pH-Änderung eine Potentialänderung bei der Mangandioxydabscheidung von 118 mV bewirkt. Bei der Permanganatbildung an der Anode wird dieselbe pH-Änderung das Elektrodenpotential um 94.4 mV verschieben (Gleichung 7). Ausserdem kommt man durch diese Betrachtung auch zu dem wichtigen Schluss, dass die Bildungspotentiale von Sauerstoff, Permanganationen und Mangandioxyd nach den obenangeführten Reaktionsgleichungen mit der Verkleinerung des pH-Wertes positiver werden, und dass das Anodenpotential bei der Mangandioxydabscheidung die grösste Änderung im positiven Sinne erleidet. Andererseits ist aus denselben Gleichungen ersichtlich, dass mit der Erhöhung der Manganionenkonzentration das Potential der Anode immer negativer wird.

Auf Grund dieser Erwägungen kann man den Schluss ziehen, dass die Abscheidung von Sauerstoff in jedem Fall stattfinden würde, wenn die Sauerstoffüberspannung nicht in Erscheinung träte. Wegen bedeutender Sauerstoffüberspannung kommt es zuerst zur Bildung von Mangandioxyd und dann von Permanganat in stark sauren Lösungen von Mangansulfat, wobei die Konzentration von Manganionen theoretisch so klein wie möglich sein sollte. Mit der Erhöhung des pH und der Konzentration von Manganionen kommt man in das Gebiet der Sauerstoffabscheidung bei positivsten Anodenpotentialen unter den gegebenen Arbeitsbedingungen. Ausserdem, da die Intensität der Änderung der Abscheidungspotentiale von Mangandioxyd, Permanganat und Sauerstoff bei gleichen pH-Änderungen eine verschiedene ist, wie oben gezeigt wurde, so wird bei der Erhöhung des pH-Wertes der Lösung die Reihenfolge der Abscheidung der einzelnen Oxydationsprodukte geändert, wobei die Abscheidung von Sauerstoff und Mangandioxyd überhandnehmen, und die Oxydation von Manganionen zu Permanganationen immer weniger in Erscheinung treten wird.

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Um diese theoretischen Betrachtungen experimentell zu prüfen, wurden die Potentiale der Arbeitsanode in wässrigen Lösungen verschiedener Konzentrationen von Schwefelsäure, Lösungen von Mangansulfat und Lösungen von Mangansulfat und Schwefelsäure verschiedenen gegenseitigen Verhältnisses wie üblich gemessen. Als Anode diente eine Platindrahtspirale oder ein Platinblech. Der Anolyt war von dem Katholyten durch ein Diaphragma aus Glasfritte oder durch einen mit Anolyten gefüllten elektrolytischen Schlüssel getrennt, um die kathodische Reduktion von gebildeten Permanganationen auszuschliessen[21]. Den Katholyten bildete wässrige Schwefelsäure mit oder ohne Zusatz von Kaliumsulfat (95 ml H_2O + 5 ml konz. H_2SO_4 + 5 g K_2SO_4). Die erhaltenen experimentellen Ergebnisse zeigt die Fig. 1, auf welcher die Potentialänderung der Anode in Abhängigkeit von der Elektrolytkonzentration und von dem gegenseitigen Verhältnis von Mangansulfat und Schwefelsäure bei verschiedenen Temperaturen aufgetragen ist. Wie ersichtlich, wird das Potential der Anode in wässrigen Lösungen von Mangansulfat verschiedener Konzentrationen schwach positiver mit Verkleinerung der Mangansulfatkonzentration, wobei nur Mangandioxyd gebildet wird. Übereinstimmend mit den Ergebnissen der theoretischen Erwä-

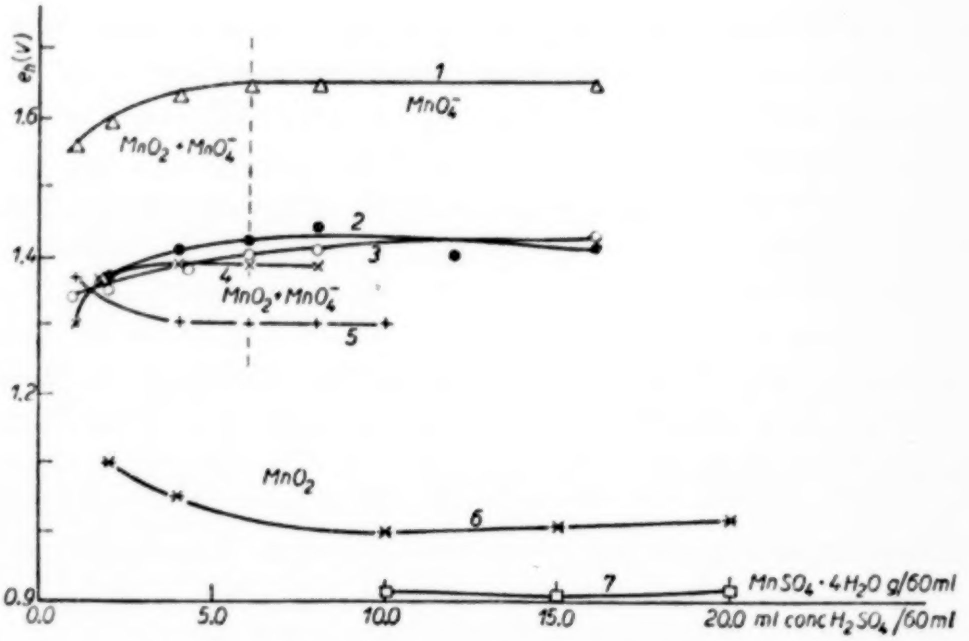

Fig. 1. Potentialänderung der Platinanode in Abhängigkeit von der Elektrolytkonzentration und von dem gegenseitigen Verhältnis von Mangansulfat und Schwefelsäure, bei verschiedenen Temperaturen.

1 H_2SO_4 var
2 1 g $MnSO_4 \cdot 4H_2O$ + H_2SO_4 var/60 ml
3 4 g $MnSO_4 \cdot 4H_2O$ + H_2SO_4 var/60 ml
4 10 g $MnSO_4 \cdot 4H_2O$ + H_2SO_4 var/60 ml
5 1 ml conc. H_2SO_4/60 ml + $MnSO_4 \cdot 4H_2O$ var
6 $MnSO_4 \cdot 4H_2O$ var
7 $MnSO_4 \cdot 4H_2O$ var (∼ 60° C)

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gungen sollte der pH-Wert verringert werden, um zu dem Abscheidungspotential von Permanganationen zu gelangen. Die Potentiale in Lösungen mit konstanten Konzentrationen von Schwefelsäure bei veränderlichen Konzentrationen von Mangansulfat sind, wegen der pH-Änderung, mit über 300 mV positiver. Dabei kommt es in sauren Lösungen neben der Mangandioxydabscheidung auch zur Bildung von Permanganat. Durch Erhöhung der Säurekonzentration bekommt das Potential der Anode immer positivere Werte und die Bildung von Permanganationen nimmt mit der weiteren Verkleinerung des pH überhand, so dass von Schwefelsäurekonzentrationen von 3.6N an und höher nur Permanganat gebildet wird, wie auch analytisch festgestellt wurde. Die auf O Amp/qcm extrapolierten Potentiale der Anode, bei welchen nur Permanganat gebildet wird, sind positiver als + 1.4 V, oder etwas negativer bei höherer Konzentration des Anolyten an Mangansulfat. Auf diese Weise wurde auch experimentell bewiesen, dass bei positiveren Potentialen als + 1.4 V in Lösungen die 3.6N und mehr an Schwefelsäure und 0.45M an Mangansulfat sind, nur Permanganat quantitativ, ohne gleichzeitige Bildung von Mangandioxyd, erzeugt wird. Da die Abscheidung von Sauerstoff aus schwefelsauren Lösungen ab etwa + 1.7 V ansetzt, bildet dieses extrapolierte positive Potential auch die obere Grenze der quantitativen Erzeugung von Permanganat, ohne gleichzeitige Abscheidung von Sauerstoff. Diese obere Grenze der positiven Potentiale ist auf der Fig. 1 durch die oberste Kurve gebildet, die die Potentialänderung bei der Abscheidung von Sauerstoff mit der Änderung der Schwefelsäurekonzentration darstellt.

Die praktischen Potentialwerte bei der Stromstärke von etwa 9 mA, der mittleren Stromstärke unserer coulometrischen permanganometrischen Bestimmungen, bei der das Permanganat quantitativ erzeugt wird, befanden sich zwischen + 1.43 und + 1.62 V.

Das Konzentrationsgebiet rechts von der vertikalen unterbrochenen Linie (Fig. 1) ist dasjenige in welchem es bei Einhaltung der angegebenen Potentialwerte und Elektrolytzusammensetzung, zur quantitativen Permanganatbildung kommt, während links von der Trennungslinie, in allen untersuchten Systemen, mit Verkleinerung der Konzentration von Schwefelsäure oder Mangansulfat die Potentiale eine ausgesprochene Tendenz nach negativeren Werten bekommen, wobei in diesem Konzentrationsgebiet die Gefahr der Bildung von Mangandioxyd und Sauerstoff immer grösser wird.

Durch wiederholte genaue Bestimmungen konnten auf diese Weise in guter Übereinstimmung mit den eingangs gemachten theoretischen Erwägungen, experimentell die Bedingungen ausgearbeitet werden, unter welchen man tatsächlich zur quantitativen Erzeugung von Permanganat gelangen kann, ohne dass es gleichzeitig zu irgendwelcher Bildung von Mangandioxyd oder Sauerstoff kommt[22]. Wie gezeigt, erwiesen sich als sehr geeignet wässrige schwefelsaure Lösungen nicht unter 3.0N, am besten von 3.6N an und höher, die zugleich etwa 0.45 bis 0.020M an Mangansulfat sind. Kleinere Mangansulfatkonzentrationen sind nicht zu empfehlen, da man schon bei Konzentrationen von 0.01M ungenaue Resultate bekommt. Dadurch wurde gleichzeitig auch eine der wichtigsten Grundbedingungen für die praktische Durchführung und Entwicklung der coulometrischen Permanganatometrie geschaffen.

ZUSAMMENFASSUNG

Um die coulometrischen permanganatometrischen Bestimmungen zu ermöglichen, wurde durch theoretische und experimentelle Untersuchungen, auf Grund des Studiums der Anodenpotentiale von Platin und der elektrolytischen Oxydationsprozesse, die Möglichkeit der quantitativen Bildung von Permanganationen in schwefelsauren, wässrigen Lösungen von Mangansulfat gefunden. Unter bestimmten Bedingungen des Anodenpotentials, der Konzentration des Anolyten und des gegenseitigen Verhältnisses von Mangansulfat und Schwefelsäure erfolgt mit verschiedenen Stromstärken eine sichere und bequeme quantitative Erzeugung von Permanganationen, die für verschiedene sekundäre Oxydationen verwendet werden können.

Auf diese Weise wurde die Grundbedingung geschaffen für die Ermöglichung und Entwicklung der coulometrischen Permanganatometrie, wodurch auch die Möglichkeit für die coulometrische Erzeugung von Permanganat und Eichung von volumetrischen auf Permanganat begründeten Standardlösungen und für weitere Anwendung des Coulombs als Ursubstanz in der Analytischen Chemie gegeben wurde.

SUMMARY

In order to realize coulometric permanganatometric determinations theoretical and experimental investigations have been carried out. By the study of anodic potentials on platinum and of electrolytic oxydation processes the possibility of the quantitative formation of permanganate ions from manganous sulfate in aqueous sulfuric acid solutions could be demonstrated. Under definite conditions of anodic potential, concentration of anolyte, and relation between manganous sulfate and sulfuric acid, by different current densities, a quantitative generation of permanganate ions can be attained, in a sure and simple manner, and can also be utilized for different secondary oxidation processes.

Thus the fundamental condition has been created for the realization and the development of the coulometric permanganatometry, and thereby the possibility of the coulometric generation of permanganate and standardization of volumetric solutions based on permanganate has also been created, as well as for the further utilization of the coulomb as a standard in analytical chemistry.

RÉSUMÉ

Les auteurs ont effectué des recherches théoriques et expérimentales pour établir des dosages permanganométriques par coulométrie. L'étude des potentiels anodiques sur platine et des processus d'oxydation électrolytique a montré la possibilité de formation quantitative d'ions permanganiques à partir de sulfate de manganèse en solution sulfurique. Dans des conditions déterminées de potentiel anodique, de concentration de l',,anolyte'' et de rapport sulfate de manganèse-acide sulfurique, pour des densités de courant différentes, les ions permanganiques peuvent se former quantitativement, de manière sûre et simple, en permettant différents processus d'oxydation secondaire. Ainsi les conditions essentielles ont été établies pour réaliser et développer la permanganométrie coulométrique permettant: la production coulométrique de permanganate, l'obtention de solutions volumétriques étalon et l'utilisation du coulomb comme étalon en chimie analytique.

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COULOMETRISCHE PERMANGANATOMETRISCHE BESTIMMUNG VON OXALAT-, FERRO- UND ARSENITIONEN *

von

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Mit elektrolytisch quantitativ erzeugten Permanganationen in schwefelsauren wässrigen Mangansulfatlösungen, die wir unlängst ausgeführt haben[1], wurden einige coulometrische permanganatometrische Titrationen, analog den volumetrischen Titrationen, ausgeführt, wodurch der Beweis der quantitativen sekundären Oxydationen durch elektrolytisch an der Platinanode in saurer Lösung erzeugtes Permanganat erbracht, und die coulometrische Permanganatometrie geschaffen wurde[2]. Dadurch wurde ausser den schon bekannten Anwendungen der coulometrischen Arbeitsweise[3] noch ein Gebiet der Analytischen Chemie eröffnet. Auf diese Weise konnte bewiesen werden, dass die coulometrische Permanganatometrie nicht nur praktisch ausführbar ist, sondern dass sie der klassischen volumetrischen Arbeitsweise gegenüber auch wertvolle Vorzüge aufweist, die nicht zu unterschätzen sind und zwar hauptsächlich deswegen, weil sie die Permanganatometrie, mit einfachen Hilfsmitteln, ohne vorherige Bereitung von Permanganatlösungen, und ausserdem mikroanalytische coulometrische Bestimmungen ermöglicht, die mit der volumetrischen Methode nicht ausführbar sind, und zwar mit einer Genauigkeit die alle Erwartungen übertrifft. Unser schon früher gemachter Vorschlag[4], das Coulomb als Ursubstanz in die gesamte Analytische Chemie und hauptsächlich in die Volumetrie einzuführen, konnte an noch einem Gebiet, an der coulometrischen Permanganatometrie erhärtet werden und es konnte der Beweis erbracht werden für die Vorzüge der coulometrischen Eichung der Standardlösungen und für die ausserordentlich exakte Permanganatometrie, ohne vorher bereitete und geeichte Permanganatlösungen.

Bei der Ausarbeitung der Arbeitsmethoden für die coulometrische permanganatometrische Bestimmung von Oxalat-, Ferro- und Arsenitionen, haben wir absichtlich die bekannten instrumentellen Methoden für die Endpunktbestimmung vermieden und genaue Bestimmungen mit Hilfe von Farbindikatoren erstrebt, mit dem Ziele, die coulometrische Permanganatometrie so einfach wie möglich zu gestalten, um von Anfang an die Bedingungen zu schaffen für ihre Einführung auch in solche analytische Laboratorien, die keine Möglichkeit oder keine grossen Erfahrungen im Gebrauch der elektrochemischen Methoden haben. Aus diesem Grunde wurden verschiedene Möglichkeiten in Betracht gezogen und es wurde in dem Feroin ein auch für die coulometrische Permanganatometrie, sehr geeigneter Indikator gefunden.

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* Vorgetragen im Rahmen des 4. Clausthaler Chemietages der Gesellschaft Deutscher Chemiker — Ortsverband Harz — in Goslar und Clausthal-Zellerfeld, 1-3 Juli 1954.

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Apparativ wurden die coulometrischen permanganatometrischen Bestimmungen, ebenso wie die coulometrische jodometrische Thiosulfatbestimmung[5] mit getrenntem Katholyten und Anolyten ausgeführt[6], wegen der möglichen Reduktion von erzeugten Permanganationen[7] und Oxalationen[8] an der Kathode. Die Bestimmungen können sowohl in zwei geeigneten, durch eine elektrolytische Brücke, als auch durch eine Glasfrittenmembran verbundenen Glasbechern, an Elektroden aus Platinblech oder Platindrahtspiralen ausgeführt, oder es wird die Platinkathode mit dem geeigneten Katholyten in einem mit Glasfritte verschlossenen röhrenförmigen Behälter unmittelbar in den Anolyten eingeführt [9,10]. Für intensives Rühren wird durch einen Glasrührer Sorge getragen, wobei auch die Möglichkeit vorgesehen ist den Anolyten während der Bestimmung mässig erwärmen zu können. Die Bestimmungen erstreckten sich hauptsächlich auf Mengen von 1 bis 8 mg der zu bestimmenden Ionen, wobei die Bestimmungen, mit Stromstärken von etwa 7 bis 20 mA, bzw. mit Stromdichten von 1.2 bis 3.4 mA/qcm, bzw. mit 3 bis 15 Coulombs, in der Zeit von 5 bis 20 Minuten zu Ende geführt werden konnten. Bei der angewandten Stromstärke von 7 mA wurden in 1 sec $7.25 \cdot 10^{-5}$ mÄq, bzw. $1.724 \cdot 10^{-3}$ mg Permanganationen, und bei 20 mA in 1 sec $2.07 \cdot 10^{-4}$ mÄq, bzw. $4.928 \cdot 10^{-3}$ mg Permanganationen erzeugt.

Der Katholyt besteht aus etwa 5%-iger wässriger Lösung von Schwefelsäure mit oder ohne Zusatz von etwa 5% Kaliumsulfat. Den Grundelektrolyten bildet wässrige schwefelsaure Lösung von Mangansulfat solcher Konzentration und solchen Verhältnisses der beiden Komponenten, dass es dabei nach den früher festgelegten Bedingungen[1] quantitativ zur anodischen Erzeugung von Permanganationen kommt, ohne auch spurenweise Abscheidung von Mangandioxyd oder Sauerstoff. Als sehr geeignet erwies sich der Grundelektrolyt etwa $3.6N$ und höher an Schwefelsäure und etwa 0.45 bis $0.025M$ an Mangansulfat, in welchem das Anodenpotential, gemessen gegen Normalwasserstoffelektrode, bei Stromstärken von etwa 7 bis 20 mA, bzw. bei Stromdichten von 1.2 bis 3.4 mA/qcm zwischen + 1.45 und + 1.62 V liegt.

COULOMETRISCHE OXALATIONENBESTIMMUNG

Auf der bekannten Reaktion von Oxalationen mit Permanganationen

$$MnO_4^- + 8\,H^+ + 5\,C_2O_4^{-2} \rightleftarrows Mn^{+2} + 10\,CO_2 + 4\,H_2O \qquad (1)$$

wurde auch die coulometrische permanganatometrische Oxalationenbestimmung begründet. Der Äquivalenzpunkt wurde durch Feroin als Farbindikator[11] genügend scharf angezeigt. Die Lösung mit dem zu bestimmenden Oxalation wird nach der Zusammenstellung der ganzen Apparatur dem Grundelektrolyten in dem Anodenraum zugegeben.

Eine unmittelbare primäre elektrolytische Oxydation von Oxalationen an der Anode wurde, in analytisch feststellbarem Ausmasse, unter den angeführten Arbeitsbedingungen, nicht beobachtet, ausser einer schwachen, teilweisen Oxydation durch anodisch gebildeten Sauerstoff[12, 13]. Ebenfalls tritt auch eine Oxydation des zu bestimmenden Oxalats durch den Luftsauerstoff[13] wohl in so geringem Ausmasse in Erscheinung, dass sie in den Grenzen unserer Arbeitsfehler gar nicht stört.

Wegen der bedeutend grösseren Reaktionsgeschwindigkeit zwischen den gebildeten Permanganationen und Feroin, als zwischen Permanganationen und den zu bestimmenden Oxalationen, kommt es infolge der Feroinoxydation bedeutend früher zur Farbänderung, noch vor der quantitativen Oxydation von Oxalationen durch elektrolytisch gebildetes Permanganat, was zu bedeutenden und variablen Fehlern führen kann, wie wir durch eingehende Untersuchungen festgestellt hatten. Durch Zusatz von Mercuriionen, in Form von Mercurichlorid, konnte, unter unseren Arbeitsbedingungen, keine Beschleunigung der Reaktion zwischen Permanganat- und Oxalationen beobachtet werden[14, 15, 16]. Auch bei fortdauernder Oxydation und wahrscheinlicher Bildung des ersten Oxydationsproduktes des Oxalations, des Oxalatoions $(COO)_2^-$, blieb die ziemlich ausgesprochene Trägheit der Oxydation erhalten, die der Schnelligkeit der angewandten Permanganationenerzeugung ihre Grenzen auflegt. Aus diesem Grunde wird die Elektrolyse des Grundelektrolyten mit den zugegebenen Oxalationen ohne vorherige Zugabe von Feroin unter strenger Einhaltung konstanter Stromstärke und genauer Zeitmessung bis zum Erscheinen von unverbrauchten Permanganationen, die sich durch ihre Farbe anzeigen, durchgeführt. Ohne den Strom zu unterbrechen wird erst dann ein genau abgemessenes Volumen, am besten 1 ml Feroinlösung (4 ml 0.025*M* *o*-Phenantrolin — Ferrosulfat + 4 ml 0.1*N* Mohr'sches Salz + 30 ml Wasser) zugegeben, dessen Konzentration und Menge so bemessen wird, dass augenblicklich das gesamte überschüssige, elektrolytisch gebildete Permanganat verbraucht wird und die Lösung eine deutlich rote Färbung annimmt. Die coulometrische Titration wird weiter bis zu der scharfen und deutlichen Farbänderung nach graublau geführt und in diesem Augenblick der Strom unterbrochen und die Zeit gestoppt, am besten automatisch beide gleichzeitig. Die Farbänderung zeigt an, dass, nach der schon erfolgten Oxydation der Oxalationen durch elektrolytisch gebildetes Permanganat, auch die Reaktion zwischen zugegebenem Feroin und immer weiter erzeugten Permanganationen beendet ist.

Die Gesamtmenge der durch den Stromkreis durchgeflossenen Coulombs entspricht, nach dem stöchiometrischen Verhältnis, dem zu bestimmenden Oxalation

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plus der Strommenge für die entsprechende Oxydation von zugegebenem Feroin. Um aus der Coulombmenge die Menge der bestimmten Oxalationen zu berechnen, muss man diejenige Coulombmenge, die für die Oxydation von zugegebenem 1 ml Feroin gebraucht wird, abziehen. Diese Coulombmenge kann vorher oder nachträglich im selben Grundelektrolyten festgestellt werden.

Es hat sich gezeigt, dass hauptsächlich bei mikroanalytischen Bestimmungen auch Spuren von oxydierbaren Verunreinigungen im Grundelektrolyten bedeutende Fehler verursachen können. Da man nie eine volle Gewissheit über das Nichtvorhandensein reduktiver Substanzen haben kann, empfiehlt es sich immer vor der Ausführung der eigentlichen Bestimmung in dem vorbereiteten Grundelektrolyten eine Blindprobe auszuführen und daraus die Elektrizitätsmenge für die Oxydation von reduktiven Substanzen, die fast immer vorhanden sind, zu berechnen und im Endresultat zu berücksichtigen.

Unter verschiedenen Bedingungen von Oxalatmenge und Konzentration, Konzentration von Schwefelsäure und Mangansulfat, Stromstärke, Temperatur und Katholytzusammensetzung ausgeführte coulometrischen permanganatometrischen Oxalatbestimmungen haben zu dem Endergebnis geführt, dass auf diese Weise Oxalationen unter verschiedenen Bedingungen, die in weiten Grenzen variieren können, einer genauen Bestimmung zugänglich sind. Optimale Stromstärken für die Bestimmung von 2 bis 10 mg Oxalationen in etwa 60 ml Lösung, liegen zwischen 7 und 20 mA, weil unter diesen Bedingungen die Farbänderung im Äquivalenzpunkt genügend scharf ist und ausserdem die Geschwindigkeit der elektrolytischen Permanganaterzeugung immer kleiner als die Reaktionsgeschwindigkeit zwischen Permanganat- und Oxalationen bleibt, wodurch die rechtzeitige Beendigung der Oxalationenoxydation nicht in Frage gestellt wird. Da die Konzentration der Schwefelsäure, wie schon gezeigt, einen ausschlaggebenden Einfluss ausübt, soll sie nicht unter $3.0N$ verkleinert werden, da es sonst leicht, wegen nicht quantitativer Permanganaterzeugung, zu ungenauen Resultaten kommen kann. Wegen der möglichen chemischen Zerlegung von vorhandenem Oxalat durch Schwefelsäure, soll auch ihre Konzentration keinesfalls höher als $4M$ sein[17]. Die Konzentration von Mangansulfat fällt nicht so sehr ins Gewicht[1] und genaue Bestimmungen können in Grundelektrolyten mit geeigneter Schwefelsäurekonzentration bei gleichzeitiger Mangansulfatkonzentration von etwa $0.45M$ bis etwa $0.025M$ ausgeführt werden. Bei weiterer Verkleinerung der Mangansulfatkonzentration läuft man jedoch Gefahr ungenaue Resultate zu bekommen, die schon bei der Konzentration von $0.014M$ bedeutend abstechen.

Die Temperatur spielt eine grosse Rolle und nur Bestimmungen bei etwa 30° und höher führten fast ausnahmslos zu genauen Resultaten, während die Resultate bei niedrigeren Temperaturen stark variierten und grösstenteils einen nicht quantitativen Reaktionsverlauf anzeigten.

Unter diesen Bedingungen konnten fast ohne Ausfall Bestimmungen mit einem Fehler von $+0.93$ bis -0.85% der genommenen Oxalatmenge ausgeführt werden,

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wie aus der Tabelle I zu ersehen ist. Der Ursprung der Fehler liegt unter anderem in der gewählten Endpunktbestimmung und in der nicht genügend genauen Abmessung der Substanzmenge und der angewandten Volumina, im Vergleich mit der ausserordentlichen Genauigkeit der Coulombabmessung, die nur von der technischen Einrichtung, die heute ungemein leistungsfähig und automatisiert ist, abhängt und die Möglichkeiten einer Massen- und Voluminaabmessung bei weitem übertrifft.

TABELLE I

Annähernde Konz. von $Na_2C_2O_4$ Mol/l	Genommen $Na_2C_2O_4$ mg	Gefunden $Na_2C_2O_4$ mg	Fehler		Stromstärke mA	Dauer der Bestimmung sec
			mg	%		
$1.53 \cdot 10^{-3}$	9.238	9.205	—0.033	—0.37	8.47	1565.0
$1.48 \cdot 10^{-3}$	8.950	8.877	—0.073	—0.85	8.48	1507.5
$1.02 \cdot 10^{-3}$	6.159	6.167	0.008	0.14	8.47	1048.7
$1.02 \cdot 10^{-3}$	6.159	6.157	—0.002	—0.03	8.47	1046.9
$9.91 \cdot 10^{-4}$	5.977	5.953	—0.024	—0.40	8.48	1011.0
$5.11 \cdot 10^{-4}$	3.079	3.066	—0.013	—0.45	8.47	521.3
$4.96 \cdot 10^{-4}$	2.988	2.966	—0.022	—0.74	8.48	506.3
$4.33 \cdot 10^{-4}$	2.611	2.615	0.004	0.03	8.47	444.0
$4.33 \cdot 10^{-4}$	2.611	2.611	0.00	0.00	8.47	443.9
$4.33 \cdot 10^{-4}$	2.611	2.616	0.005	0.19	8.47	444.7
$3.45 \cdot 10^{-4}$	2.080	2.073	—0.007	—0.33	8.47	352.4
$3.45 \cdot 10^{-4}$	2.080	2.066	—0.014	—0.67	8.47	355.3
$3.45 \cdot 10^{-4}$	2.080	2.099	0.019	0.93	8.47	366.9

COULOMETRISCHE FERROIONENBESTIMMUNG

Ausser der Methode für die Oxalationenbestimmung wurde auch die coulometrische permanganatometrische Methode für die Ferroionenbestimmung ausgearbeitet, in Anlehnung an die bekannte volumetrische Bestimmung, die auf folgendem Reaktionsverlauf begründet ist

$$5\,Fe^{+2} + MnO_4^- + 8\,H^+ \rightleftarrows Mn^{+2} + 5\,Fe^{+3} + 4\,H_2O \qquad (2)$$

Unmittelbare anodische Oxydation der Ferroionen verläuft, nach unseren Versuchen, in schwefelsaurer Lösung, auch bei längerer Elektrolyse bei verschiedenen Stromdichten nur in ganz kleinem Ausmasse, so dass auf einer einfachen anodischen Oxydation der Ferroionen ohne intermediäre Permanganationenerzeugung keine quantitative Ferroionenbestimmung aufzubauen wäre, wobei die geringfügige teilweise unmittelbare Oxydation, ohne Anwesenheit von Mangansulfat im Grundelektrolyten, nicht in Betracht kommt.

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Die coulometrische permanganatometrische Ferroionenbestimmung lässt sich nach unseren Untersuchungen mit elektrolytisch erzeugtem Permanganat unter bestimmten Bedingungen sehr leicht und genau ausführen, wobei ebenfalls, wie bei der Oxalatbestimmung, dieselben Vorteile stark in Erscheinung treten. Die Ferroionenbestimmung lässt sich noch einfacher als die Oxalationenbestimmung in demselben Grundelektrolyten ausführen. Der Unterschied besteht darin, dass dem Grundelektrolyten am Anfang der Bestimmung zuerst 2 bis 3 Tropfen Feroinlösung (*ca.* 0.025*M* *o*-phenantrolin-ferrosulfat, zugegeben und die Elektrolyse bis zur Farbänderung geführt wird, um erst dann die Lösung mit den zu bestimmenden Ferroionen zuzugeben und weiter in der schon oben beschriebenen Apparatur und unter angegebenen Bedingungen für die quantitative Erzeugung von Permanganationen zu Ende zu führen, das durch den Farbumschlag wie üblich angezeigt wird. Eine nochmalige, nachträgliche Zugabe von Feroin bei der Ferroionenbestimmung erübrigt sich, da das zuerst zugegebene und bis zur Farbänderung elektrolytisch titrierte Feroin durch die Zugabe von zu bestimmenden Ferroionen wieder befähigt wird die Rolle des Indikators zu spielen und das Ende der Reaktion zwischen Ferro- und Permanganationen anzuzeigen. Von der gesammten durchgeflossenen Strommenge muss nur die bekannte Strommenge für die Farbänderung von Feroin abgezogen werden, um zu der für die Hauptoxydation gebrauchten Strommenge, bzw. Ferroionenmenge zu gelangen.

Unter verschiedenen Arbeitsbedingungen ausgeführte Ferroionenbestimmungen haben gezeigt, dass in dem schon beschriebenen Grundelektrolyten bei Temperaturen um 30°, mit Feroin als Indikator, sehr einfach, schnell und genau auch mikroanalytische Bestimmungen ausgeführt werden können, wobei die Fehler, bei einer Menge von 1.7 bis 3.4 mg Ferroionen in etwa 60 ml Lösung, zwischen +1.11 und —0.47% lagen (Tabelle II).

TABELLE II

Annähernde Konz. von $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Genommen Fe^{+2}	Gefunden Fe^{+2}	Fehler		Strom-stärke	Dauer der Bestimmung
Mol/l	mg	mg	mg	%	mA	sec
$1.35 \cdot 10^{-3}$	3.395	3.426	0.031	0.09	8.40	704.4
$1.35 \cdot 10^{-3}$	3.395	3.394	—0.001	—0.04	8.40	697.9
$1.35 \cdot 10^{-3}$	3.395	3.402	0.007	0.18	8.40	699.6
$1.04 \cdot 10^{-3}$	2.604	2.600	—0.004	—0.15	8.37	536.6
$1.04 \cdot 10^{-3}$	2.604	2.596	—0.008	—0.31	8.37	535.7
$1.04 \cdot 10^{-3}$	2.604	2.592	—0.012	—0.44	8.37	535.0
$1.01 \cdot 10^{-3}$	2.547	2.576	0.029	1.13	8.40	529.6
$1.01 \cdot 10^{-3}$	2.547	2.546	—0.001	—0.05	8.40	523.5
$7.93 \cdot 10^{-4}$	1.994	1.996	0.002	0.10	8.41	409.9
$7.93 \cdot 10^{-4}$	1.994	1.990	—0.004	—0.21	8.41	408.7
$7.93 \cdot 10^{-4}$	1.994	1.994	0.00	0.00	8.41	409.8
$6.76 \cdot 10^{-4}$	1.698	1.703	0.005	0.31	8.40	350.4
$6.76 \cdot 10^{-4}$	1.698	1.698	0.00	0.00	8.40	349.5

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Der mögliche Einfluss des Luftsauerstoffs und die unerwünschte Oxydation der Ferroionen durch ihn[18] tritt bei diesen Bestimmungen nicht in messbaren Ausmassen in Erscheinung, ist aber bei Mikrobestimmungen durch Abschliessen des Anolyten und Arbeiten unter Stickstoff unschwer zu vermeiden.

COULOMETRISCHE ARSENITIONENBESTIMMUNG

Die Oxydation von Arsentrioxyd durch Permanganationen in saurer Lösung nach der bekannten Gleichung

$$5\,As_2O_3 + 4\,MnO_4^- + 12\,H^+ \rightleftarrows 5\,As_2O_5 + 4\,Mn^{+2} + 6\,H_2O$$

bzw.

$$5\,As_2O_3 + 10\,H_2O \rightleftarrows 5\,As_2O_5 + 20\,H^+ + 20\,e^-$$

konnten wir auch für die coulometrische Bestimmung ausnützen.

MacNevin und Martin[19] haben die Bedingungen für quantitative Oxydation von As^{+3} in As^{+5} an einer Platinanode in stark sauren Lösungen angegeben. In unserem sauren Elektrolyten verläuft diese unmittelbare Oxydation nicht glatt, während die Oxydation mittels der anodisch zwischengebildeten Permanganationen in unserem Grundelektrolyten glatt quantitativ vonstatten geht, so dass in ihm auch mikroanalytische Bestimmungen mit guter Genauigkeit ausgeführt werden können.

Die Reaktionsgeschwindigkeit zwischen den Arsenit- und Permanganationen ist, im Gegensatz zu den Geschwindigkeiten der schon angeführten Oxydationen, bedeutend kleiner, so dass unser Grundelektrolyt, der die Arsenitionen enthält, schon am Anfang der coulometrischen Titration deutlich vom erzeugten Permanganat gefärbt wird. Die erwünschte Reaktion kann, wie bekannt, durch Spuren von Jodationen soweit beschleunigt werden[20], dass die coulometrische Titration mit Stromstärken von etwa 10 mA befriedigend vonstatten geht. Die Wirkung von Jodationen ist so günstig, dass Zugabe von nur 2 Tropfen einer 0.002*M* wässrigen Lösung vom Kaliumjodat völlige Entfärbung durch vorhandenes Arsenition bewirkt und weiter eine günstige Reaktionsgeschwindigkeit unterhält. Aber auch in Gegenwart von Jodationen ist die Reaktionsgeschwindigkeit zwischen Permanganationen und Feroin bedeutend schneller, weswegen es zu vorzeitiger Farbänderung von Feroin, bzw. vorzeitiger Anzeige des Titrationsendes kommt. Aus diesem Grunde muss, auch in Anwesenheit von Jodationen, die immer noch ungenügende Reaktionsgeschwindigkeit, hauptsächlich der letzten Spuren von Arsenitionen in Betracht gezogen, und die coulometrische Titration mit einer Unterbrechung und erst nachheriger Feroinzugabe durchgeführt werden. Durch Temperaturerhöhung wird die Reaktionsgeschwindigkeit ebenfalls erhöht, so dass die Bestimmungen am besten zwischen 30° und 50° auszuführen sind. Aber auch bei Anwendung aller dieser Massnahmen kann festgestellt werden, dass der Grundelektrolyt in dem die coulometrische Titration ausgeführt wird, eine deutliche

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Färbung von überschüssigem Permanganat schon einige Minuten vor dem erwarteten Titrationsende annimmt, obwohl im Elektrolyten noch unveränderte Arsenitionen vorhanden sind. Würde man schon bei der ersten Anfärbung des Elektrolyten Feroin zugeben um auf die endgültige Farbänderung des Feroins in einem Zuge weiterzutitrieren, so würde man fast ohne Ausnahme bedeutend niedrigere Resultate erhalten. Um diesen, durch allzukleine Reaktionsgeschwindigkeit der letzten Spuren von Arsenitionen mit Permanganationen bedingten Fehler zu vermeiden, muss man nach deutlicher Färbung des Elektrolyten durch überschüssiges Permanganat den Stromkreis unterbrechen und unter stetigem Rühren etwa 10 Minuten abwarten, bis die Reaktion quantitativ zu Ende verlaufen ist, damit im Augenblicke der Zugabe von Feroin nur noch das überschüssige Permanganat im Grundelektrolyten vorhanden sei. Sollte sich die Lösung nach der Unterbrechung der Titration entfärben, so muss die coulometrische Titration ohne Zugabe von Feroin bis zu neuem Erscheinen von Permanganatüberschuss fortgesetzt und wieder auf einige Minuten ausgesetzt werden, wobei die Färbung erhalten bleiben soll. Erst nach Ablauf der nötigen Wartezeit soll 1 ml Feroin (4 ml 0.025M *o*-Phenantrolin-Ferrosulfat + 4 ml 0.1N Mohr'sches Salz + 30 ml Wasser) zugegeben und bis zur Farbänderung zu Ende titriert werden. Danach wird dasselbe Volumen Feroinlösung, meistens 1 ml, zugegeben und wieder zu Ende titriert. Von der gesamten Zeitdauer der coulometrischen Bestimmung von Arsenitionen und Feroin, ohne eine eventuelle Blindprobe mitzurechnen, wird der zweifache Betrag der Zeit, die für die coulometrische Titration der zugegebenen einzelnen Volumina der Feroinlösung benötigt wird, abgezogen und durch Multiplikation mit der konstanten Stromstärke die äquivalente Arsenit- bzw. Arsentrioxydmenge berechnet. Um auch bei der Arsenitionenbestimmung eventuell in der Grundlösung vorhandene Spuren reduktiver Substanzen von Anfang an zu entfernen, wird auch bei diesen coulometrischen Titrationen die Blindprobe ausgeführt.

Unter Beachtung der angeführten Gesichtspunkte konnten zahlreiche mikroanalytische Arsentrioxydbestimmungen in Mengen von 2 bis 5 mg in etwa 60 ml Lösung ausgeführt werden, wobei sich die Fehler, wie aus der Tabelle III ersichtlich ist, zwischen +0.62 und —0.87% bewegten.

Die erreichte Genauigkeit der Bestimmungen stellt bei weitem nicht die Grenze dar, sondern kann durch apparative Verfeinerung und automatische, sehr genaue Konstanthaltung der Stromstärke und genauere Zeitmessung noch bedeutend erhöht werden.

Durch diese Untersuchungen wurde die Möglichkeit der quantitativen elektrolytischen Permanganaterzeugung in sauren Elektrolyten aus Mangansulfat[1] analytisch ausgenützt und Methoden für quantitative coulometrische permanganatometrische Oxalat-, Ferro- und Arsenitionenbestimmung in makro- und mikroanalytischen Mengen ausgearbeitet, wodurch die coulometrische Perman-

TABELLE III

Annähernde Konz. von As_2O_3 Mol/l	Genommen As_2O_3 mg	Gefunden As_2O_3 mg	Fehler mg	Fehler %	Stromstärke mA	Dauer der Bestimmung sec
$4.66 \cdot 10^{-4}$	5.166	5.182	0.016	0.31	8.48	1192.4
$4.66 \cdot 10^{-4}$	5.166	5.198	0.032	0.62	8.48	1196.1
$4.66 \cdot 10^{-4}$	5.166	5.170	0.004	0.08	8.48	1189.1
$4.66 \cdot 10^{-4}$	5.166	5.173	0.007	0.13	8.48	1190.3
$4.66 \cdot 10^{-4}$	5.166	5.139	—0.027	—0.52	8.48	1182.2
$4.65 \cdot 10^{-4}$	5.148	5.111	—0.037	—0.71	8.45	1180.3
$4.65 \cdot 10^{-4}$	5.148	5.166	0.018	0.34	8.45	1192.8
$4.65 \cdot 10^{-4}$	5.148	5.115	—0.003	—0.64	8.45	1181.2
$4.35 \cdot 10^{-4}$	4.818	4.778	—0.040	—0.83	8.48	1099.4
$4.35 \cdot 10^{-4}$	4.818	4.824	0.006	0.20	8.48	1110.1
$2.33 \cdot 10^{-4}$	2.583	2.558	—0.025	—0.97	6.46	550.0
$2.33 \cdot 10^{-4}$	2.583	2.581	—0.002	—0.08	8.46	555.3
$2.33 \cdot 10^{-4}$	2.583	2.579	—0.004	—0.16	8.46	554.8

ganatometrie geschaffen und die reale Möglichkeit ihrer weiten praktischen Anwendung gezeigt wurde. Zu gleicher Zeit wurde, durch Schaffung der coulometrischen Permanganatometrie, noch ein Gebiet der analytischen Chemie der künftigen Abmessung und Eichung durch das Coulomb, anstelle der Abmessung von Masse, zugeführt, laut unserem Vorschlag[4,21], der schon praktische Anwendung auf andere Fälle[22] und allgemeinere Zustimmung erfahren hat[23].

ZUSAMMENFASSUNG

Auf der quantitativen elektrolytischen Permanganaterzeugung in wässrigen schwefelsauren Lösungen von Mangansulfat aufbauend, wurden coulometrische permanganatometrische Methoden für die quantitative Bestimmung von Oxalat-, Ferro- und Arsenitionen mit Endpunktbestimmung durch Farbindikatoren entwickelt. Dadurch wurde die coulometrische Permanganatometrie geschaffen und die Möglichkeit ihrer weiten praktischen Anwendung gezeigt.

Zu gleicher Zeit wurde, durch Schaffung der coulometrischen Permanganatometrie, noch ein Gebiet der analytischen Chemie der Abmessung und Eichung durch das Coulomb, anstelle von Masse der Ursubstanz, erschlossen und die Einführung von Coulomb als Ursubstanz auch weiter begründet und praktisch ermöglicht.

SUMMARY

Methods based upon the quantitative electrolytic generation of permanganate in aqueous sulfuric acid solutions of manganous sulfate have been developed for the coulometric permanganatometric determination of oxalate, ferrous, and arsenious ions; the end-point being ascertained by means of colour changes of indicators. In this way coulometric permanganatometry has been established and the possibility of its large practical utilization has been shown.

Thus, by the creation of the coulometric permanganatometry, the coulomb, replacing the mass of the standard, has penetrated into still another part of analytical chemistry for measurement and standardization.

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RÉSUMÉ

Les auteurs ont établi des méthodes pour le dosage par permanganométrie coulométrique des oxalates, du fer(II) et de l'arsenic(III), en utilisant des indicateurs pour la détermination du point final; ces méthodes sont basées sur la formation quantitative du permanganate par voie électrolytique, à partir du sulfate de manganèse en solution sulfurique. C'est ainsi qu'est née la permanganométrie coulométrique, offrant un vaste domaine d'applications pratiques. Grâce à cette permanganométrie coulométrique, le coulomb peut alors remplacer les substances étalon au cours des titrations.

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BUCHBESPRECHUNG

Theoretische Grundlagen der Organischen Chemie, von WALTER HÜCKEL, 2. Band, 6 und 7 Auflage, Akademische Verlagsgesellschaft Geest und Portig K.G., Leipzig, 1954, 801 Seiten, 72 Abb., DM. 21.80.

Schon die erste Auflage dieses Werkes hat sich in der Bibliothek jedes Organikers einen bleibenden Platz erobert, der durch die folgenden Auflagen noch gefestigt wurde. Nach dem Kriege mußten allerdings für ähnliche Fragestellungen die moderneren angelsächsischen Monographien zu Rate gezogen werden. Durch die Neuauflage des zweiten Bandes, in dem die Literatur bis 1951/52 verarbeitet ist, hat nun das gesamte Werk seinen alten Aktionsradius wiedergewonnen, sodaß ihm zumindest seine frühere Stellung sicher ist.

Ein besonderes Charakteristikum dieses Buches ist die kritische Art der Darstellung, die nicht die Meinung einer oder mehrerer Schulen vorträgt, sondern in umfassender Weise zeigt, wo unsere theoretischen Anschauungen aus sicheren experimentellen Unterlagen hervorgehen, und wo die Hypothesen anfangen. Zugleich erhält der Leser ein eindringliches Bild vom Wert und der Anwendungsbreite der verschiedensten Methoden.

Diese Darstellungsweise bringt es mit sich, daß die früheren Auflagen lediglich veraltet, aber nicht fehlerhaft sind. Die neuen Ergebnisse sind — zwar auf Kosten der Prägnanz — lediglich als Erweiterungen um über 100 Seiten in den Text eingearbeitet, „weil es für jeden, der sich für das Werden wissenschaftlicher Erkenntnis interessiert, von Wert ist zu sehen, wie sich die . . . aufgestellten Theorien im Laufe der Zeit gewandelt haben und was von ihnen schließlich heute noch geblieben ist."

Im Einzelnen sind in die beiden Hauptabschnitte *Konstitution und physikalische Eigenschaften* und *Konstitution und Reaktionsgeschwindigkeit* die folgenden Ergebnisse neu aufgenommen bzw. ausführlicher erörtert worden:

Die Sublimationswärme des Kohlenstoffs als Grundlage zur Berechnung der Energie der C-C-Bindung; die Grundlage und Anwendung der Dielektrika-Theorie von ONSAGER UND KIRKWOOD, die Methoden zur Erforschung der Molekülform und die Kalottenmodelle; UR-Methoden zur Erforschung der Assoziation; neue Ergebnisse der Röntgen-Strukturanalyse. Die Verfahren der Endgruppen- und Gestaltbestimmung hochmolekularer Polysaccharide sind stark ergänzt worden, während die gleichen Probleme beim Eiweiß noch nicht berücksichtigt sind. Die Näherungsverfahren zur Berechnung der Mesomerie-energie ungesättigter und aromatischer Systeme sind besonders ausführlich diskutiert, desgleichen die Biradikale mit ihrem magnetischen Verhalten. Tiefgreifend ist der Abschnitt über aromatische Substitution verändert worden, in dem anschließend an die alten statischen Theoriern (z.B. von VORLÄNDER) die modernen dynamischen Vorstellungen ausführlich entwickelt werden. Bei den Erklärungsversuchen des MILLS-NIXON-Effektes tritt die kritische Einstellung des Verfassers besonders hervor.

Erfreulicherweise ist auch ein Abschnitt über Polymerisation durch Kettenreaktionen aufgenommen worden.

Neben diesen vielseitigen Ergänzungen wird der Wert dieses Buches noch durch besonders zahlreiche Literaturzitate und vorzügliche Register erhöht. Der niedrige Preis macht sich teilweise in der Qualität von Druck und Papier bemerkbar.

S. HÜNIG (Marburg)

STUDIES ON DERIVATIVES OF 8-HYDROXYQUINOLINE (OXINE). THE SENSITIVITY AND SELECTIVITY OF 5-NITROSO-OXINE AND 2-METHYL-5-NITROSO-OXINE TOWARDS THE GROUP IIIB METALS

by

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INTRODUCTION

Oxine has proved itself to be a most versatile organic reagent for the detection and determination of many metals[1], but owing to its extreme 'unselectivity' its usefulness has been somewhat marred. It has been known for many years that the introduction of specific groupings in the oxine structure, both in the pyridine and phenolic rings causes an increase in the selectivity towards certain metals. To this end the 2-methyl derivative was examined by MERRITT AND WALKER[2], who found that the substitution of a methyl group in position 2 introduced the possibility of steric hindrance, so that the reagent did not chelate with aluminium under the conditions in which chelation occurred with the parent compound.

Recently[3] it has been found that the introduction of a nitroso group in position 5 also causes an increase in selectivity in oxine. 5-Nitroso-oxine does not give a precipitate with aluminium under specific conditions. The increased acidity of the molecule attendant on the presence of the nitroso group may be a possible explanation for this anomalous behaviour.

As the introduction of both these groups individually into the oxine structure causes an increase in selectivity, a natural extension of this investigation would be to examine the effect that the introduction of both a methyl and a nitroso group in the same oxine structure would have. As the Group IIIB metals form a well defined series, the reactions of 5-nitroso-oxine and 2-methyl-5-nitroso-oxine towards aluminium, yttrium, gallium, indium and thallium(III) have been investigated.

EXPERIMENTAL

Preparation of reagents

5-Nitroso-oxine

This compound has been described by VON KOSTANECKI[4] and a modification to this method has been proposed by ALBERT AND MAGRATH[5]. Samples of the desired material were prepared by both these methods and compared. In both cases the final product, after repeated recrystallizations from ethyl alcohol, still had an indefinite melting point. However, the material prepared by ALBERT AND MAGRATH's method appeared to have a slightly narrower softening range (230 to 235° C) and was therefore chosen for use. Chromatographic analysis of samples showed the material to be substantially homogeneous.

2-Methyl-5-nitroso-oxine

This compound was prepared by the direct nitrozation of the 2-methyl derivative derivative by the following method.

5.3 g of 2-methyl-oxine was dissolved in 9 ml of 10*N* hydrochloric acid, cooled to 0° C and treated dropwise with a solution of 2.5 g of sodium nitrite dissolved in 9 ml of water. After the addition of most of the nitrite, 2-methyl-5-nitroso-oxine hydrochloride began to precipitate from solution. The mixture was stirred for 1 hour after the addition of the nitrite solution, allowed to stand for 24 hours in a refrigerator, then filtered, sucked as dry as possible *in situ*, washed three times with 5 ml portions of ice water, again sucked as dry as possible, dissolved in 90 ml of *N* sodium carbonate solution, heated to 60 to 70° C and neutralized by the addition of 1.1 ml of glacial acetic acid. The free base was allowed to stand for 24 hours, then filtered using a sintered glass filter, washed with 200 ml of ice cold 1 : 1 alcohol/diethyl ether and dried overnight at 50° C to give 2.6 g of yellow orange material.

The melting point of a sample recrystallized three times from ethyl alcohol was 213° C (w.d.). Found $N = 14.91\%$; $C_{10}H_8O_2N_2$ requires $N = 14.89\%$.

Reagent solutions

The two reagent solutions were prepared by dissolving the material in absolute ethyl alcohol to give an *M*/50 solution. For purposes of comparison *M*/50 solutions of oxine and 2-methyl-oxine were also prepared.

Metal solutions

The metal solutions were initially *M*/100 and were prepared from aluminium ammonium sulphate, gallium and indium metal, yttrium nitrate and thallic oxide. The thallic oxide was previously dried for 1 hour at 150° C, cooled in a desiccator, dissolved in concentrated sulphuric acid with the addition of 2 drops of concentrated hydrochloric acid, taken to moist dryness and taken up in water. Redistilled water was used in all cases.

Buffer solutions

Buffer Solutions A, B and C having pH's of 5.3, 8.35 and 13.1 respectively were prepared as previously described[6]. The pHs were measured using a Doran pH meter Model 4980 and a lithium glass 'alk-acid' electrode assembly through the range 0-14.

Sensitivity tests

These were carried out as previously described[6] using the method based on that of LUTZ[7] employed by IRVING *et al*[8]. In this method the sensitivity of a reagent is recorded in terms of the smallest amount of metal which will give a perceptible precipitate in a fixed volume of test solution under standard conditions. The results obtained are expressed by the term pL, which is defined as $-\log_{10}$ limiting concentration, in gram equivalents per litre, for the volumes of metal solution V_1 and V_2 within which the limit of detection lies. As previously explained[6, 8], this value is preferred as an expression of sensitivity, as the use of μg per ml, as usually employed, may convey a false impression of the difference in sensitivities of the reagent with metals of differing atomic weight or valency.

RESULTS

The results obtained for oxine, 5-nitroso-oxine, 2-methyl-oxine, and 2-methyl-5-nitroso-oxine are given in Tables I to IV respectively.

TABLE I

SENSITIVITY LIMITS USING OXINE

Metal	Molarity M	Buffer	$V_1 — V_2$ ml	pL	Remarks
Al^{+3}	0.01	A	0.4-0.3	3·24-3·37	
Al	0.01	B	0.4-0.3	3·24-3·37	
Al	0.01	C	NP*†	—	
Y^{+3}	0.01	A	NP**	—	
Y	0.01	B	—	—	Metal blank ppts. at this pH
Y	0.01	C	—	—	,, ,,
Ga^{+3}	0.01	A	—***	—	Metal blank ppts.
Ga	0.001	B	0.2-0.1	4·54-4·84	
Ga	0.01	C	NP	—	
In^{+3}	0.01	A	0.2-0.1****	3·54-3·84	
In	0.01	B	0.2-0.1	3·54-3·84	
In	0.01	C	NP	—	
Tl^{+3}	0.001	A	0.3-0.2	4·37-4·54	
Tl	0.001	B	0.3-0.2	4·37-4·54	
Tl	0.01	C	—	—	Metal ppts.

* With high concentrations of Al no precipitation occurs, *cf.* IRVING *et al.* who consider that the metal is held up as complex ions with oxine.

** With high concentrations of Y no precipitation occurs (*vide supra* note*).

*** Precipitation occurs, but the limit is indefinite, owing to precipitation of the metal blank at this pH.

**** With high concentrations of In no precipitation occurs, (*vide supra* note*)

† NP = No precipitate.

TABLE II

SENSITIVITY LIMITS USING 5-NITROSO-OXINE

Metal	Molarity	Buffer	$V_1 - V_2$	pL	Remarks
Al^{+3}	0.01	A	NP†	—	See note*
Al	0.01	B	NP	—	
Al	0.01	C	NP	—	
Y^{+3}	0.01	A	NP	—	
Y	0.01	B	—	—	Metal blank ppts.
Y	0.01	C	—	—	Metal blank ppts.
Ga^{+3}	0.01	A	—	—	Metal blank ppts.
Ga	0.01	B	NP	—	
Ga	0.01	C	NP	—	
In^{+3}	0.01	A	NP	—	
In	0.01	B	NP	—	
In	0.01	C	NP	—	
Tl^{+3}	0.01	A	indefinite	—	See note**
Tl	0.01	B	NP	—	
Tl	0.01	C	—	—	Metal blank ppts.

* Although the metal blank precipitates at high concentrations, no precipitate is obtained when the reagent is present. The metal is held up, presumably as complex ions with 5-nitroso-oxine (*vide supra* Table I).

** Precipitation occurs with Tl in Buffer A but the limit is indefinite, but would appear to lie between 0.4 and 0.3 ml of 0.001 M Tl. With higher concentrations of Tl no precipitation occurs (*cf.* Note*).

† NP = No precipitate.

TABLE III

SENSITIVITY LIMITS USING 2-METHYL-OXINE

Metal	Molarity	Buffer	$V_1 - V_2$	pL	Remarks
Al^{+3}	0.01	A	NP†	—	
Al	0.01	B	NP	—	
Al	0.01	C	NP	—	
Y^{+3}	0.01	A	NP	—	
Y	0.01	B	—	—	Metal blank ppts.
Y	0.01	C	—	—	Metal blank ppts.
Ga^{+3}	0.001	A	—	—	Metal blank ppts.
Ga	0.001	B	0.4-0.3	4.24-4.37	
Ga	0.001	C	NP	—	
In^{+3}	0.001	A	indefinite	—	
In	0.001	B	0.3-0.2	—	
In	0.01	C	0.4-0.3	3.24-3.37	
Tl^{+3}	0.001	A	0.2-0.1	4.54-4.84	
Tl	0.0001	B	0.4-0.3	5.24-5.37	
Tl	0.01	C	—	—	Metal blank ppts.

† NP = No precipitate.

TABLE IV

SENSITIVITY LIMITS USING 2-METHYL-5-NITROSO-OXINE

Metal	Molarity	Buffer	$V^1 - V^2$	pL	Remarks
Al^{+3}	0.01	A	NP†	—	
Al	0.01	B	NP	—	
Al	0.01	C	NP	—	
Y^{+3}	0.01	A	NP	—	
Y	0.01	B	—	—	Metal blank ppts.
Y	0.01	C	—	—	Metal blank ppts.
Ga^{+3}	0.01	A	—	—	Metal blank ppts.
Ga	0.01	B	NP	—	
Ga	0.01	C	NP	—	
In^{+3}	0.01	A	NP	—	
In	0.01	B	NP	—	
In	0.01	C	NP	—	
Tl^{+3}	0.01	A	NP	—	
Tl	0.01	B	NP	—	
Tl	0.01	C	—	—	Metal blank ppts.

† NP = No precipitate.

DISCUSSION

From the above tables it may be clearly seen that greatly increased selectivity occurs on the introduction of methyl and nitroso groups in the oxine structure. With oxine, precipitation occurs with all the Group IIIB metals. Aluminium is held up in alkaline solution through the concentration range examined. At a pH of 5.3 no precipitation occurs with the higher concentrations of aluminium. This has been observed by IRVING *et al*[8]. who offer the explanation that the metal is held up in the form of complex ions with oxine. This anomaly also occurs with the higher concentrations of yttrium. With yttrium in Buffer B some precipitation of complex occurs, but the limit is unreliable due to precipitation of the metal itself at this pH.

Gallium is precipitated by oxine at pH 5.3 but again the limit is indefinite due to precipitation of the metal at this pH. No precipitation occurs from very alkaline solutions. Indium is precipitated by oxine in acid and neutral buffers, but no precipitation occurs at pH 13.1. It is of interest to note that with higher concentration of the metal no precipitation occurs, doubtless due to the formation of complex ions with oxine. The same behaviour occurs with thallium in high concentrations, but in this case at a pH of 8.35. The limit in Buffer C is unreliable due to precipitation of the metal.

Table II shows the greatly increased selectivity of 5-nitroso-oxine. No precipitation occurs with aluminium, yttrium, gallium and indium under the conditions of the tests. Although aluminium precipitates out from high concentrations in Buffer A no precipitation occurs when the reagent is present. Although yttrium precipitates out in Buffers B and C, no difference is detectable between the metal blanks and the tubes containing metal and reagent.

With thallium in Buffer A, no precipitation occurs at high concentrations of the metal, but precipitation takes place at lower concentrations, the tubes exhibiting a slight fluorescence. No precipitation occurs at pH 8.35, and the limit is indefinite at pH 13.1 due to precipitation of the metal itself. With 2-methyl-oxine a lesser degree of selectivity is obtained. The reagent does not precipitate aluminium as noted by MERRITT AND WALKER[2]. Yttrium is not precipitated under these conditions, but precipitation occurs with gallium, indium and thallium.

With gallium, precipitation occurs at pH 8.35, but the metal is held up in solution at pH 5.3 and 13.1.

With indium, precipitation occurs at pH 5.3, but the limit is indefinite. With Buffer B at pH 8.35 however, 2-methyl-oxine shows its maximum sensitivity, the limit lying between 0.3 and 0.2 ml of 0.001M metal solution. The sensitivity is greatly reduced at pH 13.1.

Precipitation occurs with thallium in Buffers A and B. Greatest sensitivity is shown in Buffer B where the limit lies between 0.4 and 0.3 ml of 0.0001M metal solution. The reagent shows its greatest sensitivity towards any group IIIB metal with thallium at this pH.

With 2-methyl-5-nitroso-oxine no precipitation occurs with any metal at any pH. The reagent does not prevent precipitation of the metal itself in those cases where it will precipitate on the addition of the buffer solution. The four reagents show a very interesting gradation in selectivity with respect to the Group IIIB metals. With 5-nitroso-oxine the increased acidity due to the nitroso group may well account for this increase in selectivity. With 2-methyl-5-nitroso-oxine both steric hindrance and increased acidity would appear to contribute to the selectivity.

It is remarkable that the sensitivity remains constant with these reagents and metals. Taking a pL value of 4.2 as average[8], the average pL value for 2-methyl-oxine with the Group IIIB metals is 4.4 and that for oxine 3.94.

It has been observed[9] that, with very few exceptions, the average pL value for any derivative with any series of metals is extremely near to the value of 4.2 quoted by IRVING. Although individual variations in pL values may naturally occur, a change of ± 1.0 is rather unusual. 2-Methyl-oxine follows the general pattern with gallium, but appears somewhat less sensitive towards indium. The average pL value of 5.3 for thallium (III) and 2-methyl-oxine is, however, unusual. No explanation may be offered for this behaviour with the existing state of knowledge regarding sensitivity.

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SUMMARY

2-Methyl-5-nitroso-8-hydroxyquinoline (2-methyl-5-nitroso-oxine), hitherto undescribed, has been prepared. The sensitivity and selectivity of this oxine derivative, together with 5-nitroso-oxine, and 2-methyl-oxine towards aluminium, yttrium, gallium, indium and thallium(III) have been investigated. A gradation in selectivity is found. With oxine, precipitation occurs with all the above metals under the conditions of the test. With 2-methyl-oxine, precipitation occurs with all metals with the exception of aluminium. With 5-nitroso-oxine, no precipitation occurs with aluminium, yttrium, gallium and indium, and with 2-methyl-5-nitroso-oxine, no precipitation occurs with any metal in Group IIIB. A possible explanation for this behaviour is advanced.

ZUSAMMENFASSUNG

Es wird die Darstellung von 2-Methyl-5-nitroso-8-oxychinolin (2-Methyl-5-nitroso-oxin), welche bisher in der Literatur noch nicht erwähnt worden ist, beschrieben. Die Empfindlichkeit und Selektivität des 2-Methyl-5-nitroso-oxins sowie auch des 2-Methyl-und des 5-Nitroso-oxins in Bezug auf Al, Y, Ga, In und Tl(III) wurden untersucht. Die Selektivität zeigte eine Steigerung. Alle obengenannten Metalle bilden einen Niederschlag mit Oxin unter den gegebenen experimentellen Bedingungen. Das 2-Methyloxin gibt keinen Niederschlag mit Al, 5-Nitroso-oxin gibt keinen Niederschlag mit Al, Y, Ga und In, während das 2-Methyl-5-nitroso-oxin mit überhaupt keinem Metall der Gruppe IIIB reagiert. Eine mögliche Erklärung für diese Erscheinung wird gegeben.

RÉSUMÉ

On a effectué la synthèse de la 2-méthyl-5-nitroso-8-hydroxyquinoléine (2-méthyl-5-nitroso-oxine), non encore décrite dans la littérature. La sensibilité et la sélectivité de ce composé ont été examinées, de même que celles de la 5-nitroso-oxine et de la 2-méthyl oxine vis-à-vis de Al, Y, Ga, In et Tl(III). Ces réactifs présentent une gradation dans leur sélectivité. Bien que l'oxine donne des précipités avec tous les métaux mentionnés ci-dessus, même dans les conditions d'expérience, la 2-méthyloxine ne précipite pas Al, le dérivé nitrosé ne précipite pas Al, Y, Ga et In et la 2-méthyl-5-nitroso-oxine ne précipite pas les métaux du groupe III B. Une explication en est donnée.

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A STUDY OF THE REPRODUCIBILITY OF ANALYTICAL BALANCES

by

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In using an analytical balance, an operator attempts to estimate the equilibrium state of the balance under the specified load. The agreement of a series of such estimates made under a given set of conditions is the reproducibility of the balance. Knowledge of balance reproducibility is useful in (1) evaluating the analytical error due to the balance and (2) evaluating the balance as a weighing instrument. Although analytical balance reproducibility is often discussed in a general way, there has been little quantitative evaluation or treatment of it; thus its application has been limited.

In the present investigation, the authors have studied in particular the variation of reproducibility as a function of sensitivity.

Under a given set of conditions the total variance of a balance arises from a number of sources, among which are (1) reading error, (2) mechanical error, (3) operator error, and (4) environmental error. The first two are inherent to the balance and the last two are more or less controllable by the operator. If the environmental and operational errors are maintained small and uniform, they may be included in the mechanical error. The total balance variance is then the sum of variances due to readability and to mechanical sources, represented as follows:

$$\sigma_t^2 = \sigma_m^2 + \sigma_r^2 \tag{1}$$

in which σ^2 is the variance, *i.e.*, the square of the standard deviation, and subscripts t, m, and r denote total, mechanical and reading errors, respectively. Equation (1) may be given in scale units, *e.g.*, divisions designated by a subscript (div) or in mass units, milligrams, designated by a subscript (mg). The two statistics are related through the sensitivity S, *i.e.*, $\sigma_{(\mathrm{div})} = \sigma_{(\mathrm{mg})} S$, where S is in div/mg).

As will be shown, the indeterminacy at lowest sensitivities is almost entirely due to the reading error, hence $\sigma_r > \sigma_m$. At highest sensitivities, the reverse situation prevails with the mechanical error predominating, *i.e.*, $\sigma_m > \sigma_r$. Accordingly, an experimental survey of balance reproducibility over a wide range of sensitivities affords estimation of these two balance characteristics.

EXPERIMENTAL ANALYSIS OF BALANCE REPRODUCIBILITY

In this study, the sensitivity was varied by adjusting the sensitivity bob. For each rest point determination the beam was released first, then the pans. (This order was reversed in the study of one balance, as noted in the succeeding section.) Riders or chains were not adjusted between rest points. Rest points were taken in groups of eleven replicates. At most sensitivity settings, groups of eleven replicates were taken at each of two rider (or chain) settings. From this data, reproducibility estimates with twenty degrees of freedom were calculated and also the sensitivity. (Sensitivities in this paper refer to change in the rest point in scale divisions per milligram.)

Three balances were tested in the present study. All were nearly new, having undergone only limited usage, and each balance was from a different manufacturer. Two of the balances, Balances A and B, were chain-type balances priced in the \$ 300- \$ 400 range. The load limit of Balance A was stated to be 200 g and of Balance B 100 g. Balance C was not chain-type and cost \$ 100- \$ 150. Sensitivities were given by the manufacturers to be 1/20 mg for Balances A and B and 1/10 mg for Balance C.

RESULTS AND DISCUSSION

Data obtained on the three balances at zero load are summarized in Fig. 1. Reproducibilities are given in mass units and show clearly the region of constant values at the higher sensitivity. These estimates, especially those at the highest sensitivities are only slightly affected by readability and may properly be considered an estimate of the mechanical error of the balance. In this sense, the high sensitivity reproducibility is a criterion of quality of balance design and workmanship. The mechanical errors for Balances A and C are approximately four

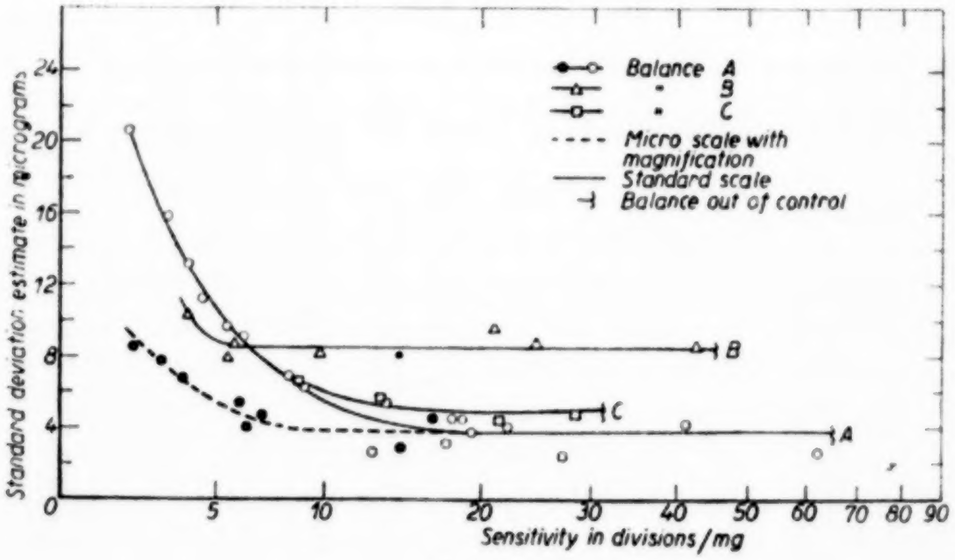

Fig. 1

to five μg with Balance A showing slight superiority. It is unexpected that the performance of Balance C, which markets for less than half the price of Balance A, should approach the performance of Balance A so nearly. Balance B is unexpectedly inferior in mechanical reproducibility. In part, its shortcoming is attributed to the release mechanism.

The low sensitivity range is the range to which analytical balances are adjusted by the manufacturer and in which most balances are used. In this range, reproducibility in mass units drops rapidly with increase of sensitivity (Fig. 1). In linear units, however, the reproducibility is a constant over a considerable range, clearly indicating readability as the controlling factor for this region. Illustrative data taken on Balance A are given in Table I. A few reproducibility estimates were made in the low sensitivity region on Balances B and C. They agreed closely with those of Balance A and indicated that, in general, balances used for usual weighings under usual conditions have the same effectiveness with respect to reproducibility regardless of price.

To study further the relationship of readability to reproducibility in the low sensitivity region, the regular scale on Balance A (1 div = 1 mm) was replaced with a microscale (1 div = 0.033 mm) and a 3× magnifier. Data with the microscale and magnifier are given in Table II and reveal the effectiveness of this system in making available the potential reproducibility of the balance, namely, the mechanical reproducibility. The dashed curve in Fig. 1 further illustrates this and points out that reproducibilities approaching the maximum are available at low sensitivities and thereby without sacrifice to long periods associated with high sensitivities. (The implications of high reproducibilities of analytical balances for micro and semi-micro weighing will be treated elsewhere by the authors.)

TABLE I

REPRODUCIBILITIES OF REST POINTS AT LOW SENSITIVITIES

(s is standard deviation estimate based on twenty degrees of freedom)

Sensitivity	s(div)	s(mg)
2.0	0.040	0.020
3.3	0.050	0.015
4.0	0.055	0.014
4.5	0.050	0.011
5.5	0.055	0.010
6.0	0.060	0.010
6.5	0.060	0.009
8.0	0.065	0.008
9.0	0.055	0.006

TABLE II

REPRODUCIBILITIES OF REST POINTS AT LOW SENSITIVITIES

(With micro scale and magnification)

Divisions on micro scale = 0.033 mm
Divisions on macro scale = 0.1 mm
Magnification = 3×
(s is standard deviation estimate based on twenty degrees of freedom)

Sensitivity div (mic. scale)/mg	$s_{(div)}$ Micro scale	$s_{(div)}$ Macro scale equivalent	$s_{(mg)}$
6.0	0.060	0.020	0.010
10.0	0.08	0.027	0.008
12.0	0.09	0.030	0.0075
12.0	0.11	0.035	0.009
18.0	0.09	0.030	0.005
19.5	0.075	0.025	0.004
20.0	0.085	0.028	0.004

CONCLUSIONS

1. The reproducibility of rest points is a valuable criterion for evaluation of analytical balance performance and for comparisons of balances.

2. The reproducibility may be broken into components: (1) reading error (readability), (2) mechanical error (primarily due to agates and release mechanisms), (3) operator error, and (4) environmental error.

3. If the balance is used by a skilled operator under proper environmental conditions, the last two errors are small and constant and can be included in the "mechanical error" category for purposes of balance evaluation and comparison.

4. Experimental resolution of balance reproducibility is possible from reproducibility estimates (standard deviation of rest points from their mean) taken over a wide range of balance sensitivities, *i.e.*, estimates of readability and mechanical error can be obtained.

5. a. At very low sensitivities, the reproducibility in scale units, $s_{(div)}$, is a constant and is an estimate of the scale readability.

b. By replacement of the regular scale with a microbalance scale and magnifying lens, the reproducibility in mass units, $s_{(mg)}$, is substantially improved at low sensitivities and $s_{(div)}$ is again a constant over this range.

6. At highest sensitivities, the reproducibility in mass units, $s_{(mg)}$, is a constant and is an estimate of mechanical reproducibility.

7. For purposes of evaluation of balance performance, the reproducibility at low sensitivity is limited because it reflects only balance readability. It is a corollary of this statement, that analytical balances in a wide range of prices

perform equally well for weighing the usual loads at usual analytical balance sensitivities with respect to reproducibility.

8. The mechanical error estimate affords a criterion of quality of balance design and workmanship.

9. Reproducibilities adequate for weighings in the micro to semi-micro region are available on analytical balances by properly increasing sensitivity or at lower sensitivities by replacing the regular scale with a micro scale and magnifier.

10. The reproducibility estimate is a criterion of balance performance closely related to the reliability of the analytical result. For a more general evaluation of balance quality and performance, other tests are necessary.

SUMMARY

The variation of balance rest point reproducibility over a wide range of sensitivities is surveyed. At low sensitivities, the reproducibility in scale units is a constant. The weighing reproducibility in milligram units in this region is limited by the readability of the scale and may be improved by increasing balance sensitivity or replacing the regular scale with a micro scale and magnifier. As the sensitivity is increased above a certain limit, control of milligram reproducibility passes from scale readability to the mechanical error of the balance. At high sensitivities, reproducibility in milligram units is practically constant and this constant is a criterion of the mechanical character of the balance.

RÉSUMÉ

Les variations de reproductibilité du zéro d'une balance sont étudiées, dans un vaste domaine de sensibilités. Aux faibles sensibilités, la reproductibilité, exprimée en divisions de l'échelle, est une constante; dans cette région, la reproductibilité de la pesée, en milligramme, est limitée par la lisibilité de l'échelle; elle peut être améliorée en augmentant la sensibilité de la balance ou en remplaçant l'échelle ordinaire par une micro-échelle, munie d'une loupe. Lorsque la sensibilité est augmentée au-delà d'une certaine limite, la reproductibilité en mg n'est plus contrôlée par la lisibilité de l'échelle mais par l'erreur mécanique de la balance. Pour des sensibilités élevées, la reproductibilité en mg est pratiquement constante et cette constance est un critère de la qualité mécanique de la balance.

ZUSAMMENFASSUNG

Die Autoren haben die Variationen der Reproduzierbarkeit des Nullpunktes einer Waage studiert, und zwar in einem grossen Bereiche von Sensibilitäten. Bei kleinen Empfindlichkeiten ist die Reproduzierbarkeit eine Konstante, sofern sie in Unterteilungen der Skala ausgedrückt wird. In diesem Bereiche ist die Reproduzierbarkeit der Wägung in mg ausgedrückt, begrenzt durch die Ablesbarkeit auf der Skala. Sie kann erhöht werden durch Erhöhung der Empfindlichkeit der Waage oder indem man die gewöhnliche Skala durch eine Mikroskala ersetzt und diese mit einer Lupe versieht. Sofern die Sensibilität über eine bestimmte Grenze erhöht wird, ist die Reproduzierbarkeit nicht mehr durch die Ablesbarkeit auf der Skala bestimmt, sondern durch den mechanischen Fehler der Waage. Für hohe Empfindlichkeiten ist die Reproduzierbarkeit in mg praktisch konstant und diese Konstanz ist ein Kriterium für die Qualität der Mechanik einer Waage.

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TITRATIONS WITH EXTRACTIVE END-POINTS
II. THE DICHROMATE TITRATION

by

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INTRODUCTION

The triphenylmethylarsonium cation has been suggested as a means of extracting permanganate ions into an organic layer at the end-point of the titration of iron (II), arsenite and oxalate with potassium permanganate[1]. This paper deals with its application in a similar manner to the titration of iron (II) with potassium dichromate.

In the absence of coloured ions (except chromium (III) ions formed in the reaction) this end-point is usually determined using internal indicators such as diphenylamine sulphonate, N-phenylanthranilic acid or the more expensive tris-1 : 10-phenanthroline ferrous sulphate[2]. The characteristic colour change of these indicators at the end-point is however masked by coloured ions such as copper (II), nickel (II), cobalt (II) and large quantities of chromium (III). In such cases, potentiometric titrations[3,4] are usually employed.

The method here reported is suggested as an improvement on the more generally convenient internal indicator titration, and is recommended for the determination of iron in alloy steels with a high content of chromium, nickel, copper or cobalt, since these metals do not interfere.

DISCUSSION

A stable, bright yellow-orange crystalline compound, triphenylmethylarsonium dichromate (A) has been isolated. It is only slightly soluble in chloroform, but more soluble in ethylene dichloride and readily so in tetrachlorethane.

The extractive potassium dichromate titration with the aid of (A) is similar to the permanganate titration with triphenylmethylarsonium permanganate as indicator[1], the end-point being indicated by the colourless organic layer turning yellow due to the extraction of (A). The colour is readily seen against a white background, and is not influenced by the colour of the aqueous layer due to chromium(III) ions or added coloured cations.

The method was successfully applied to the titration of iron(II) with potassium dichromate (*N*/10) in the presence of cobalt(II), nickel(II), copper(II), chromium (III) and manganese(II) ions, as their sulphates, and chloride ions, in concentrations up to 50 times the molar concentration of iron(II). This maximum was set, not by the method, but by the solubilities of the added metal sulphates. The lightness of the extracted colour (yellow) prevented the use of dichromate solutions of lower concentrations than *N*/10.

The results obtained by the extractive method were compared with those obtained by potentiometric titration[3] and visual titration with diphenylamine as indicator[5]. Results (Table I) show that the use of the internal indicator is restricted to solutions of low chromium concentration and colourless ions such as manganese (II) and chloride.

Several alloys (containing iron, chromium, nickel and cobalt) have been successfully analysed for iron, usually without the necessity of removing the coloured ions, and the results compared with those obtained by standard methods[7,8](Table II). In the case of Risdale 10 and Bureau Analysed Samples, No. 34, the copper was removed with zinc wire or as copper sulphide to prevent deposition of copper on the Jones reductor[6]. Sulphuric acid, not hydrochloric acid[6], was used in the solution reduced, as the zinc tetrachloro complex forms an insoluble salt with the quaternary arsonium ion[9]. For a similar reason, stannous chloride was unsatisfactory for the reduction of the iron.

Both $Ph_3MeAsCl$ and $Ph_3MeAsNO_3$ (each 5 to 10 ml of 5% solution) were satisfactory salts of the Ph_3MeAs^+ cation for use in this method. Larger volumes of these solutions gave identical blanks (0.06 ml) with no change in the sensitivity. Volumes of 2 ml and less gave vague end-points.

If chloroform is used as the extractive solvent, the blank is high and the end-point vague, presumably due to the low chloroform/water distribution coefficient of (A). Ethylene dichloride and tetrachlorethane were both satisfactory, the blank being 0.06 ml, and the end-point sharp, in both cases. The former is cheap and readily available.

Solutions *N* to 2*N* with respect to H_2SO_4 gave satisfactory results; it was not necessary to add phosphoric acid to the solution as is recommended for titration with diphenylamine sulphonate as indicator[2], since the redox potential of the Fe(II)/Fe(III) couple did not have to be lowered.

EXPERIMENTAL

Triphenylmethylarsonium dichromate, $(Ph_3MeAs)_2Cr_2O_7$(A). Pure $Ph_3MeAsNO_3$ (10.0 g) dissolved in distilled water (100 ml) was added at room temperature to excess A.R. potassium dichromate (8.0 g) dissolved in 0.5*N* sulphuric acid (200 ml). A yellow-orange oil separated, and solidified on standing for five minutes. The solid was extracted with pure tetrachlorethane (50 ml), dried with anhydrous sodium sulphate, and on addition of dry light petroleum (60-90°), crystalline (A) was precipitated. The yield of (A) was quantitative only if extracted as above, since it is somewhat soluble in water. (A) was recrystallized from dry tetrachlorethane and light petroleum and dried at room temperature (6 hours) and then at 56° C (2 hours), both over P_2O_5 at 0.5 mm.

Calculated for $(Ph_3MeAs)_2Cr_2O_7$: C = 53.16%; H = 4.23%; As = 17.45%; Cr = 12.11%.

Found: C = 52.94%; H = 4.38%; As = 17.47%, 17.49%; Cr = 12.14%, 12.18%.

Procedure

The titrations were carried out in a special stoppered conical flask (500 ml) as described in the paper on the permanganate titration[1].

In all cases a 25 ml aliquot of standard ferrous ammonium sulphate solution was pipetted into the titration flask, then *N* sulphuric acid (about 200 ml) was added, together with 5% aqueous $Ph_3MeAsCl$ (10 ml) and 5 ml of ethylene dichloride (which had previously been purified by shaking with $KMnO_4$ solution, then concentrated H_2SO_4, then fractionating). The interfering cations (as their sulphates) and chloride ions (as sodium chloride) were dissolved in the *N* H_2SO_4. The potassium dichromate was added slowly with shaking near the end-point, which was indicated by the colourless ethylene dichloride changing to yellow.

TABLE I

Interfering Ion	Molar Ratio Interfering Ion: Fe (II)	Mean Titration (ml)		
		Potentiometric	Extractive	Internal Indicator
Cr^{+3}	1 : 1	24.99	25.00	25.00
Cr^{+3}	10 : 1	25.01	25.00	25.02
Cr^{+3}	50 : 1	25.02	25.02	—*
Cu^{+2}	1 : 1	25.01	25.02	—*
Cu^{+2}	10 : 1	25.01	25.01	—*
Cu^{+2}	50 : 1	25.02	25.01	—*
Ni^{+2}	1 : 1	25.00	25.00	—*
Ni^{+2}	10 : 1	25.02	25.02	—*
Ni^{+2}	50 : 1	25.03	25.03	—*
Mn^{+2}	1 : 1	25.03	25.04	25.05
Mn^{+2}	10 : 1	25.02	25.02	25.03
Mn^{+2}	50 : 1	25.04	25.04	25.05
Co^{+2}	1 : 1	25.01	25.01	—*
Co^{+2}	10 : 1	25.03	25.03	—*
Co^{+2}	50 : 1	25.05	25.04	—*
Cl^-	1 : 1	25.00	25.00	25.03
Cl^-	10 : 1	25.02	25.01	25.03
Cl^-	50 : 1	25.04	25.04	25.05

* = End-point could not be seen.

RESULTS

Table I contains the results of titration of $N/10$ ferrous ammonium sulphate with $N/10$ potassium dichromate, prepared according to VOGEL[6]. In the table, results obtained by the extractive method are compared with those obtained potentiometrically and by visual titration using diphenylamine in sulphuric acid as internal indicator.

TABLE II

COMPARATIVE RESULTS ON SAMPLES OF ANALYSED FERROUS ALLOYS

Name of Alloy	Nature of Alloy	Analysis Supplied	Iron Content Extractive Method	Standard Method	Standard Method Reference
Risdale 10	Manganese Bronze	1.84%	1.83%	1.83%	(7)
Bureau of Analysed Samples Ltd. No. 33	Alloy cast iron	91.38%*	91.11%	91.06%	(8)
Bureau of Analysed Samples Ltd. No. 34	Austenitic iron	70.90%*	70.75%	70.68%	(8)
Risdale 41G	Zinc concentrate	8.15%	8.09%	8.08%	(8)

* Calculated by difference.

SUMMARY

A method for the titration of iron(II) with $K_2Cr_2O_7$ in coloured solutions is reported, using the extraction of $Cr_2O_7^{-2}$ ions as $(Ph_3MeAs)_2Cr_2O_7$ at the end-point. The method is applicable to titration with $N/10$ $K_2Cr_2O_7$ in the presence of normally interfering coloured cations in molar concentrations up to 50 times that of the iron(II). The method may be used to estimate iron in ferrous alloys, usually without separation from the other metals present. A stable dichromate, $(Ph_3MeAs)_2Cr_2O_7$ has been isolated.

RÉSUMÉ

Une méthode est proposée pour le dosage du fer(II) au moyen de $K_2Cr_2O_7$, en solutions colorées; au point d'équivalence, les ions $Cr_2O_7^{-2}$ sont extraits sous forme de $(Ph_3MeAs)_2Cr_2O_7$. Ce procédé peut être utilisé pour des titrations au moyen de $K_2Cr_2O_7$ $N/10$ en présence d'ions colorés, gênant habituellement, en concentrations molaires allant jusqu'à 50 fois celle du fer(II). On peut ainsi doser le fer dans ses alliages, sans séparation. Un dichromate stable, répondant à la formule $(Ph_3MeAs)_2$-Cr_2O_7 a été isolé.

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ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen um Eisen(II) mit $K_2Cr_2O_7$ in gefärbten Lösungen zu bestimmen. Die Ionen $Cr_2O_7^{-2}$ werden im Umschlagspunkt in Form von $(Ph_3MeAs)_2Cr_2O_7$ ausgezogen. Dieses Verfahren kann für Titrationen mit $K_2Cr_2O_7$ *N*/10 angewendet werden in Anwesenheit von gefärbten Ionen, welche in molaren Konzentrationen bis 50 mal derjenigen des Eisens(II) normalerweise stören. Auf diese Art kann man das Eisen in Legierungen ohne Trennung bestimmen. Ein stabiles Bichromat wurde isoliert, welches der Formel $(Ph_3MeAs)_2Cr_2O_7$ entspricht.

ACKNOWLEDGEMENT

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ANALYTICAL APPLICATIONS OF THE REACTION OF THORIUM WITH BENZENEPHOSPHONIC ACID *, **

by

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For many years various organic arsonic acids have been developed and used analytically[1]. It was considered to be of interest and value to investigate analogous phosphonic acids. This work was a study of the reaction of thorium with benzenephosphonic acid and its acid derivatives.

EXPERIMENTAL

Materials

Hydrated thorium nitrate obtained from the Lindsay Chemical Company, West Chicago, Illinois, was recrystallized from water. Aqueous solutions were standardized by the classical oxalate method[2]. Filtered aqueous solutions of benzenephosphonic acid, Eastman Practical grade, m.p. 161° C, were prepared. Potentiometric titrations with standard alkali were used to standardize the solutions and showed the two end-points to require very nearly the same amount of base. The average ratio of the second to the first end-point in four titrations was 2.003 ± 0.016.

Pyrolysis curves of the thorium-benzenephosphonic acid compound

Samples of the thorium compound, precipitated with benzenephosphonic acid or phosphobenzene, the anhydro compound of benzenephosphonic acid, were heated at the rate of 6° C per minute from 100 to 1000° C. Temperature adjustment of the vertical tube furnace used was made manually by adjusting a variable transformer. Each sample, in a porcelain crucible, was suspended from the automatic recording balance of BROWN *et al.*[3] Table I presents the data.

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TABLE I

FIRST PYROLYSIS EXPERIMENT

Reagent	Temp. ranges of stability (°C)	Fraction of original ppt. wt	Wt ppt. per g atom Th
Benzenephosphonic acid (average of 2 results)	100—240	1.000	(598)*
	300—450	0.965	578
	650—800	0.762	455
	1000	0.719	430
Phosphobenzene (average of 3 results)	100—240	1.000	(598)
	300—450	0.971	581
	600—850	0.778	468
	1000	0.719	430

* Values in parentheses calculated assuming that the initial compound was $Th(C_6H_5PO_3)_2 \cdot 3H_2O$.

A second pyrolysis experiment was performed on samples in which known amounts of thorium were quantitatively precipitated with benzenephosphonic acid. Ignitions were carried out at several temperatures including those corresponding to the decomposition temperatures observed in the first pyrolysis experiment. Table II shows the data.

TABLE II

SECOND PYROLYSIS EXPERIMENT

Drying or ignition temp. (°C)	% Th	Wt ppt. per g atom Th	No. of results average
120	38.60	601.2 ± 4.2	14
150	38.76	598.9 ± 2.2	22
250	39.96	578.5 ± 4.2	4
500	50.12	461.3 ± 3.2	4
900	54.36	425.3 ± 2.6	5
1000	54.40	425.1 ± 2.4	9
1200	54.66	424.4 ± 0.8	3

Titrimetric study

Two conductimetric titrations of thorium nitrate with benzenephosphonic acid showed a 2 : 1 ratio of the reagent to thorium in the reaction involved. The endpoint observed in titrations of benzenephosphonic acid with thorium with bromophenol blue as indicator, in 50 % alcohol, from pH 3 to 4.5 substantiate the 2 : 1 ratio. The indicator apparently acts as an adsorption indicator. The titrimetric data are shown in Table III.

TABLE III

TITRIMETRIC STUDY

Sample	mmoles $Th(NO_3)_4$	mmoles $H_2C_6H_5O_3$	$\frac{\text{mmoles } H_2C_6H_5O_3}{\text{mmoles } Th(NO_3)_4}$
		Conductimetric	
1	0.479	0.901	1.88
2	0.191	0.409	2.14
		Adsorption Indicator	
3	0.0259	0.0501	1.93
4	0.0854	0.167	1.96
5	0.119	0.234	1.97
6	0.168	0.334	1.99
7	0.202	0.401	1.99
8	0.233	0.468	2.01
9	0.292	0.584	2.00
10	0.417	0.835	2.00

Quantitative precipitating and drying procedure

A series of tests showed that an easily filtered thorium precipitate was formed with benzenephosphonic acid by precipitation and digestion in 1 : 3 hydrochloric acid. Phosphobenzene yielded a similar thorium compound but not of superior quality. The diamide and dianilide of benzenephosphonic acid precipitated when glacial acetic acid solutions of the reagents were added to the aqueous sample solutions. The dimethyl ester of benzenephosphonic acid yields, on digestion with thorium in 1 : 3 hydrochloric acid, a very dense precipitate of considerably higher molecular weight than that observed with the free acid.

Precipitation of thorium (0.02 to 0.2 g) in about 150 ml of a hot hydrochloric acid solution with benzenephosphonic acid was chosen as the basis of a gravimetric method. After digestion for one hour the suspensions were diluted to about 400 ml, the pH adjusted with ammonia, the solutions filtered and the precipitates washed with hydrochloric acid of a pH similar to that of the solutions and finally dried and weighed. A series of precipitations was carried out in this manner, the pH being varied in 0.5 pH unit increments from 0.5 to 3.5. The precipitates were dried for 3 hours at 110, 120, *etc.* to 190° C. A nine-fold excess of reagent was used. Sample data in Table IV indicate that the drying temperature should be from 140 to 180° C. In each case the filtrates were made basic with ammonia and no precipitate of hydrous thorium oxide was observed even after standing a week. To establish the low extreme of the pH range another set of precipitations was performed at pH 0.5 and 0.1. These precipitates, even though dried at only 120° C, illustrate that precipitation is not complete at the lower pH. Positive tests for thorium in the filtrates were observed with ammonia in those cases where pH 0.1 was used but not in those where pH 0.5 was employed. Table IV includes this information.

TABLE IV

DRYING TEMPERATURE AND pH STUDY

pH	Sample wt (g Th)	Wt ppt. dried at (°C)								
		110	120	130	140	150	160	170	180	190
0.1	0.08868		0.2241							
0.5	0.08868	0.2290	0.2280	0.2273	0.2271	0.2268	0.2268	0.2267	0.2267	0.2260
1.0	0.08868	0.2272	0.2261	0.2256	0.2254	0.2252	0.2252	0.2251	0.2251	0.2245
1.5	0.08868	0.2266	0.2265	0.2262	0.2260	0.2259	0.2260	0.2260	0.2259	0.2258
2.0	0.08868	0.2309	0.2300	0.2285	0.2279	0.2278	0.2282	0.2280	0.2280	0.2270
2.5	0.08868	0.2290	0.2273	0.2261	0.2259	0.2258	0.2260	0.2259	0.2260	0.2259
3.0	0.08868	0.2281	0.2279	0.2276	0.2275	0.2274	0.2275	0.2274	0.2273	0.2273
3.5	0.08868	0.2286	0.2283	0.2282	0.2280	0.2279	0.2280	0.2279	0.2279	0.2278

The necessary amount of excess reagent was established by a series of experiments in which the amount of reagent was varied from a 1.7-to a 13.8-fold excess. The pH adjustment was made to 0.5 and 120° C was the drying temperature. The data in Table V indicate that a four-fold or greater excess is adequate. Testing of the filtrates with ammonia completely substantiated this.

The recommended procedure is as follows: 1. Place the sample solution containing 0.02 to 0.2 g of thorium in a 600-ml beaker. 2. Add a 150-ml portion of a 1:3 hydrochloric acid solution. 3. Heat to boiling. 4. Add a five-fold excess of benzenephosphonic acid as a 2.5 % aqueous solution. 5. Boil one hour. 6. Dilute to about 400 ml. 7. Adjust the pH to 0.5 to 1.0 with concentrated ammonia and let settle a few hours. 8. Filter into coarse filter crucibles. 9. Dry at 150° C to constant weight. 10. The gravimetric factor for thorium is 0.38796.

Analysis of the thorium-benzenephosphonic acid compound

The percentage of thorium could be calculated from the known amounts of this element used in precipitations known to be quantitative for thorium.

TABLE V

EXCESS REAGENT STUDY

No. of results	Amount excess reagent	Wt ppt. per g atom Th
1	13.8×	598.7
1	10.3×	594.3
3	8.7×	599.3
1	8.3×	598.3
2	5.9×	592.4
1	4.6×	594.5
2	4.2×	601.2
2	3.3×	588.7
1	1.7×	586.4

A Karl Fischer water determination of the dried (150° C) thorium compound by the benzene azeotrope distillation method[4] showed essentially no water.

Benzenephosphonate was determined in the dried (150° C) material spectrophotometrically by a comparison of solutions of the dried compound in concentrated hydrochloric acid with solutions prepared from standard thorium chloride and standard benzenephosphonic acid solutions with a molar ratio of reagent to thorium of 2 : 1. Absorbances in 1 cm silica cells were observed at 264.6 mμ with a Cary recording spectrophotometer.

Phosphorus was determined as phosphate in the thorium-benzenephosphonic acid compound ignited at 1200° C. Samples were fused with potassium bifluoride in platinum and taken up in concentrated hydrofluoric acid while warm. The thorium fluoride was removed by centrifugation. The fluoride solution containing the phosphate was evaporated to dryness with concentrated perchloric acid. The residue was taken up in water and titrated potentiometrically with standard base. The difference between the two end-points observed was equivalent to the phosphate in the sample. The method was proved on a U. S. Bureau of Standards primary standard sample of disodium hydrogen phosphate, the observed average analysis on three samples being 21.8 % P as compared to the theoretical value of 21.82 %.

The phosphorus to thorium ratio in the thorium-benzenephosphonic acid precipitate was shown titrimetrically to be 2 : 1. From the thorium and phosphorus analyses in Table VI it can readily be shown that the ratio remains 2 : 1 even in the material ignited at 1200° C.

$$\frac{\%\text{P}\ (232.1)}{(30.98)\ (\%\text{Th})} = \frac{14.6\ (232.1)}{(30.98)\ (54.65)} = 2.00 \qquad (1)$$

TABLE VI

ANALYSES OF THORIUM-BENZENEPHOSPHONATE COMPOUNDS

Sample dried at (°C)	Proposed formula	Molecular weight	% Th	%$C_6H_5PO_3^{-2}$	%H_2O	%P
150	$Th(C_6H_5PO_3)_2 \cdot 3H_2O$	(598.3)*	(38.79) 38.76 ± 0.15	(52.18) 52.4 ± 0.1	(9.03) 0.8 ± 0.3	
250	$Th(C_6H_5PO_3)_2 \cdot 2H_2O$	(580.3)	(40.00) 39.90 ± 0.29			
500	$Th(HPO_4)_2 \cdot 3H_2O$	(460.1)	(50.43) 50.12 ± 0.35			
1200	$Th(HPO_4)_2$	(424.1)	(54.73) 54.65 ± 0.10			(14.61) 14.6 ± 0.1

* Values in parentheses calculated from proposed formulas.

It follows that the phosphorus to thorium ratio is 2 : 1 throughout the entire series of ignition products.

Table VI gives theoretical analyses of proposed formulas and the corresponding observed analyses. The water determination indicates that no water is given up by the hydrated compound under the conditions of the experiment. This is in agreement with the observed difficulty in removing the water by ignition. The remainder of the analytical data support the formulas suggested.

Gravimetric determination of thorium as thorium-benzenephosphonate 3-hydrate

Using the recommended gravimetric procedure the results in Table VII were obtained. An interference study including thirty different cations is summarized in Table VIII. A further study of rare earth interference was made and is included in Table IX.

TABLE VII

GRAVIMETRIC DETERMINATION OF THORIUM AS $Th(C_6H_5PO_3)_2 \cdot 3H_2O$

Sample no.	Wt Th taken, g	Wt ppt., g	Wt Th found, g	Error, mg Th
1	0.06651	0.1712	0.06642	—0.09
2	0.08868	0.2268	0.08799	—0.70
3	0.1109	0.2856	0.1108	—0.1
4	0.06651	0.1704	0.06612	—0.39
5	0.1109	0.2836	0.1100	—0.9
6	0.04434	0.1154	0.04477	+0.43
7	0.04434	0.1151	0.04465	+0.31
8	0.04434	0.1142	0.04431	—0.03
9	0.06651	0.1703	0.06607	—0.44
10	0.06651	0.1716	0.06657	+0.06
11	0.08868	0.2279	0.08842	—0.26
12	0.08868	0.2309	0.08858	—0.10
13	0.08868	0.2293	0.08896	+0.28
14	0.1109	0.2861	0.1110	+0.1
15	0.1109	0.2858	0.1109	±0.0
16	0.1109	0.2883	0.1119	+1.0
17	0.1109	0.2852	0.1107	—0.2
18	0.1060	0.2735	0.1061	+0.1
19	0.1060	0.2734	0.1060	±0.0
20	0.2120	0.5484	0.2128	+0.8
21	0.2120	0.5498	0.2133	+1.3
22	0.1060	0.2742	0.1064	+0.4

TABLE VIII

INTERFERENCE STUDY OF THE GRAVIMETRIC DETERMINATION OF THORIUM AS $Th(C_6H_5PO_3)_2 \cdot 3H_2O$

Interfering substance	Interfering cation, moles/mole Th	Wt Th taken, g	Wt Th found, g	Error, mg Th
NaCl	2	0.1060	0.1066	+0.6
KCl	2	0.1060	0.1062	+0.2
$AgNO_3$	2	0.1060	0.1087	+2.7
Tl_2SO_4	2	0.1060	0.1153	+9.3
$BeCl_2$	1	0.1060	0.1067	+0.7
$Mg(ClO_4)_2$	1	0.1060	0.1064	+0.4
$CaCl_2$	1	0.2120	0.2127	+0.7
$SrCl_2$	1	0.2120	0.2143	+2.3
$BaCl_2$	1	0.1060	0.1060	±0.0
$CuSO_4$	1	0.2120	0.2136	+1.6

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TABLE VIII (CONTINUED)

Interfering substance	Interfering cation, moles/mole Th	Wt Th taken, g	Wt Th found, g	Error mg Th
$ZnCl_2$	1	0.2120	0.2134	+1.4
$CdCl_2$	1	0.2120	0.2140	+2.0
$Hg(NO_3)_2$	2	0.1060	0.1060	±0.0
$Ti(SO_4)_2$	0.25	0.2120	0.2664	+54.4
$Pb(NO_3)_2$	0.5	0.2120	0.2133	+1.3
$MnCl_2$	0.5	0.2120	0.2130	+1.0
$Co(NO_3)_2$	0.5	0.2120	0.2135	+1.5
$Ni(NO_3)_2$	0.5	0.2120	0.2132	+1.2
$Al(ClO_4)_3$	1.0	0.1060	0.1060	±0.0
$La(ClO_4)_3$	0.25	0.2120	0.2138	+1.8
Na_3AsO_3	0.5	0.2120	0.2134	+1.4
Na_3SbO_3	0.5	0.2120	0.2475	+35.5
$Bi(NO_3)_3$	0.5	0.2120	0.2126	+0.6
$Fe_2(SO_4)_3$	0.5	0.2120	0.2858	+73.8
$CrCl_3$	0.5	0.2120	0.2132	+1.2
$ZrO(ClO_4)_2$	0.25	0.2120	0.2609	+48.9
$Ce(ClO_4)_3$	0.25	0.2120	0.2131	+1.1
$SnCl_4$	0.5	0.2120	0.2911	+79.1
$VOCl_2$	1.0	0.1060	0.1070	+1.0
$UO_2(ClO_4)_2$	0.5	0.2120	0.2241	+12.1

TABLE IX: A STUDY OF RARE EARTH INTERFERENCE

Interfering substance	Amount interfering cation, g	Wt Th taken	Wt Th found	No. of results	Error, mg Th
$La(ClO_4)_3$	0.025	0.2120	0.2138	2	+1.8
$Ce(ClO_4)_3$	0.025	0.2120	0.2131	2	+1.1
$Ce(NO_3)_3$	0.025	0.1060	0.1075	3	+1.5
$Ce(NO_3)_3$	0.050	0.1060	0.1069	3	+0.9
$Ce(NO_3)_3$	0.100	0.1060	0.1088	3	+2.8
$Ce(NO_3)_3$	0.150	0.1060	0.1114	3	+5.4
$Ce(NO_3)_3$	0.200	0.1060	0.1119	3	+5.9
$Ce(NO_3)_3$	0.250	0.1060	0.1197	3	+13.7
(Mixture of	0.105	0.1060	0.1189	1	+12.9
Ce, La, Sm,	0.210	0.1060	0.1244	1	+18.4
Pr, Nd, Er, Yb)	0.315	0.1060	0.1666	1	+60.6
*$Ce(NO_3)_3$	0.200	0.1060	0.1072	2	+1.2
*None		0.1060	0.1052	1	−0.8
†$Ce(NO_3)_3$	0.200	0.1060	0.1078	2	+1.8
†None		0.1060	0.1056	1	−0.4
″$Ce(NO_3)_3$	0.200	0.1060	0.1065	1	+0.5

* 1 g citric acid added prior to precipitation.

† 0.5 ml of Fe(III)-Specific Versene (Versenes, Inc., Framingham, Mass.) was added prior to precipitation.

″The precipitation was made in twice the recommended volume of solution.

The gravimetric method for thorium is proposed as a means of determining thorium in the presence of reasonably small amounts of rare earth ions and bismuth. Larger amounts, however, interfere even in the presence of citric acid or Fe(III)-Specific Versene.

Ionization constants of benzenephosphonic acid

These constants were calculated by classical methods[5] from potentiometric titrations of doubly recrystallized benzenephosphonic acid with base using a Beckman, model G, pH meter. The ionic strength was maintained at 1.0 by appropriate addition of $4M$ sodium perchlorate at the beginning and during the titration. The results in Table XI are an average of values from two titrations for nine and ten pH values, respectively, for $\mathrm{p}K_1'$ and $\mathrm{p}K_2'$.

Spectrophotometrically determined $\mathrm{p}K'$ values were obtained from the absorbance-pH data in Fig. 1. The pH of solutions of doubly recrystallized benzenephosphonic acid was adjusted with perchloric acid or sodium hydroxide and the ionic strength was adjusted with sodium perchlorate to a value of 1.0. The pH values were measured with a Beckman, model G, pH meter. The spectra were observed with a Cary recording spectrophotometer and the absorbances calculated at 263.4 mμ. The analytical concentration of benzenephosphonic acid in each solution was $0.002497M$, determined potentiometrically.

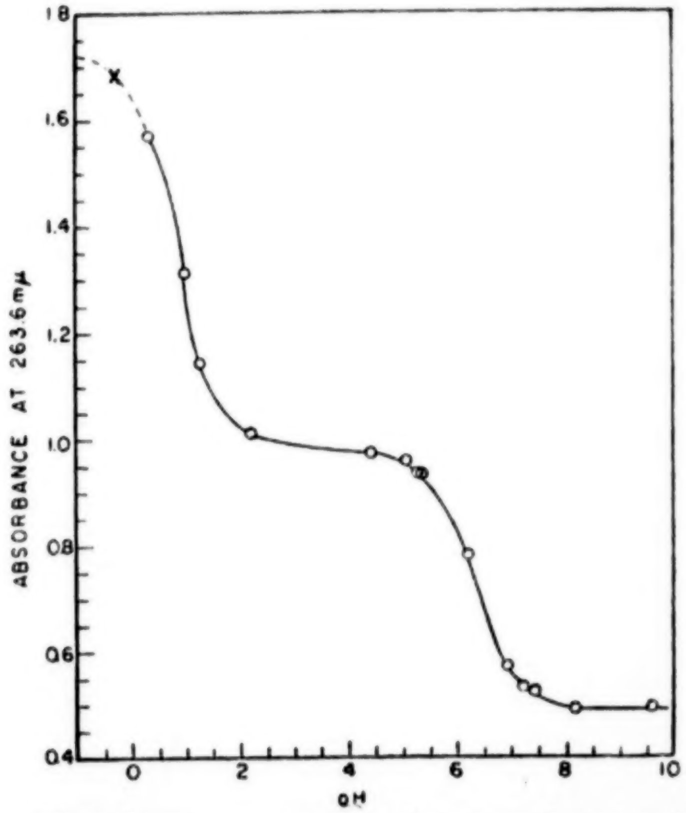

Fig. 1. Absorbance *vs.* pH for benzenephosphonic acid.

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The molar absorptivity at 263.4 mμ, ε_3, of $C_6H_5PO_3^{-2}$ can be calculated directly from the absorbances observed at pH values 8.16 and 9.60. The molar absorptivity, ε_2, of $C_6H_5PO_3H^-$ can be similarly calculated from a graphical determination of the midpoint of the absorbance break in Fig. 1, corresponding to the species $C_6H_5PO_3H^-$. Proper treatment of the following equations:

$$K_2' = \frac{a_{H^+} \, (C_6H_5PO_3^{-2})}{(C_6H_5PO_3H^-)} \tag{2}$$

$$A/b = \varepsilon_2 \, (C_6H_5PO_3H^-) + \varepsilon_3 \, (C_6H_5PO_3^{-2}) \tag{3}$$

$$0.002497 = (C_6H_5PO_3H^-) + (C_6H_5PO_3^{-2}) \tag{4}$$

$$\varepsilon_2 = 394 \text{ liters/mole-cm} \tag{5}$$

$$\varepsilon_3 = 197 \text{ liters/mole-cm} \tag{6}$$

leads to:

$$1/(0.986 - A/b) = \frac{a_{H^+}}{1.48 \, K_2'} + 0.678. \tag{7}$$

From the slope of a plot of $1/(0.986 - A/b)$ *vs.* a_{H^+}, pK_2' in Table X was calculated.

Values of pK_1' and ε_1 were calculated which are consistent with each other and with the absorbance-pH data available. A combination of the following equations:

$$K_1' = \frac{a_{H^+} \, (C_6H_5PO_3H^-)}{(C_6H_5PO_3H_2)} \tag{8}$$

$$A/b = \varepsilon_1 \, (C_6H_5PO_3H_2) + \varepsilon_2 \, (C_6H_5PO_3H^-) \tag{9}$$

$$0.002497 = (C_6H_5PO_3H_2) + (C_6H_5PO_3H^-) \tag{10}$$

with Equation (5) yields:

$$a_{H^+} = \frac{K_1' \, (0.002497) \, (\varepsilon_1 - 394)}{(0.002497 \, \varepsilon_1 - A/b)} - K_1'. \tag{11}$$

Estimated values of ε_1 predicted by the potentiometrically determined K_1' were inserted into Equation (11). For each insertion a plot of a_{H^+} *vs.*

$1/(0.002497\ \varepsilon_1 - A/b)$ was prepared and the corresponding value of pK_1' was determined from the intercept on the a_{H^+} axis.

Values of pK_1' corresponding to estimated ε_1 values were also determined graphically. At the position where absorptivity was equal to $(\varepsilon_1 - \varepsilon_2)/2$, $(C_6H_5PO_3H_2)$ was equal to $(C_6H_5PO_3H^-)$ and it also follows from the definition of K'_1 that,

$$K_1' = a_{H^+}$$
$$pK_1' = pH$$

TABLE X

CALCULATED pK_1' VALUES FOR ESTIMATED ε_1 VALUES

Estimated ε_1	pK_1 (intercept method)	pK' (A *vs.* a_{H^+} method)
695	0.89	0.96
690	0.96	0.96
685	1.03	0.97
680	1.08	0.97
675	1.15	0.97
670	1.24	0.97

TABLE XI

pK' VALUES OF BENZENEPHOSPHONIC ACID

pK'	Potentiometric	Spectrophotometric
pK_1'	0.91 ± 0.02	0.96 ± 0.03
pK_2'	6.41 ± 0.10	$6.51 + 0.02$

Values of pK_1', corresponding to estimated ε_1 values, derived by the two methods described are given in Table X. It is shown that the best agreement in calculated pK_1' values occurs at $\varepsilon_1 = 690$ liters/mole-cm.

Potentiometrically determined pK' values have been reported by LESFAURIES *et al.*[6] ($pK_1' = 1.60$, $pK_2' = 6.85$) and by JAFFÉ *et al.*[7] ($pK_1' = 1.83$, $pK_2' = 7.07$). The ionic strength was maintained at a value of 1.0 in this work and apparently ignored in the previous work. The values reported in this paper are substantiated by two independent experimental methods.

Absorption spectra of benzenephosphonic acid and derived ionic species

The absorption spectra in the range 250 to 290 mμ of benzenephosphonic acid in perchlorate solutions of ionic strength one at pH values 9.61 and 8.16 previously discussed in reference to pK' determinations, gave directly the absorption spectra of $C_6H_5PO_3^{-2}$.

The spectra observed at pH 4.43 was corrected for the $C_6H_5PO_3^{-2}$ present to yield the spectra of $C_6H_5PO_3H^-$. The corrections of ε_2 at various wavelengths were made by means of Equation (3) which follows from Beer's law, the assumption that absorbances are additive and that the amount of the species $C_6H_5PO_3H_2$ is insignificant at pH 4.43. The values of ε_3 at various wavelengths were taken from the spectra at high pH, the relative concentrations of the two species involved were determined from Equation (3) by insertion of values of A, ε_2 and ε_3 at 263.4 mμ which were previously determined in connection with the pK' determinations.

In a strictly analogous fashion the spectra observed at pH *ca.* —0.3 was corrected to yield the spectra of $C_6H_5PO_3H_2$. The spectra are shown in Fig. 2 and Table XII.

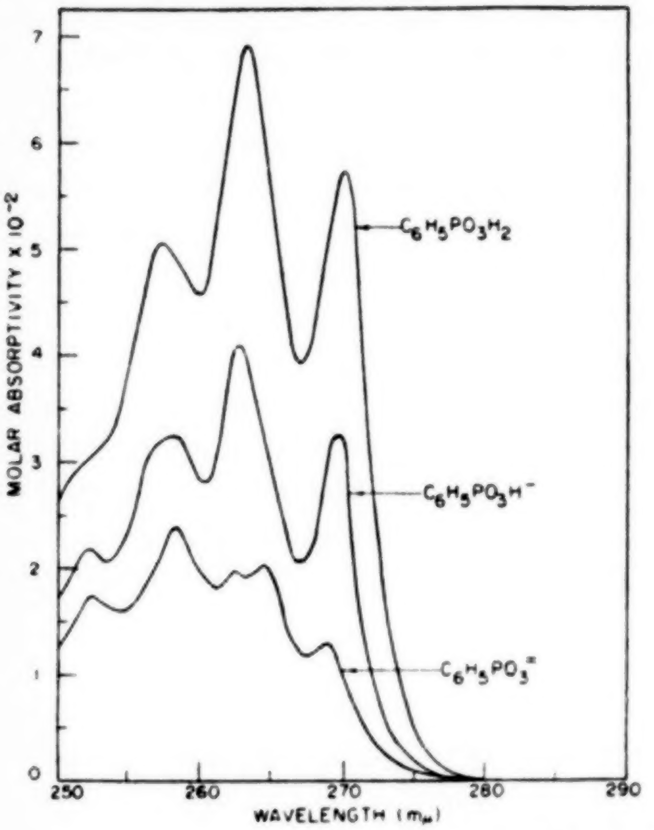

Fig. 2. Absorption spectra.

TABLE XII

ABSORPTION SPECTRAL DATA FOR BENZENEPHOSPHONIC ACID AND DERIVED IONIC SPECIES

$C_6H_5PO_3^{-2}$		$C_6H_5PO_3H^-$		$C_6H_5PO_3H_2$	
(mμ)	ε_{max}	(mμ)	ε_{max}	(mμ)	ε_{max}
252.4	174	252.2	218	257.3	505
258.4	242	258.1	325	263.6	690
262.5	197	262.7	416	—	—
264.6	202	—	—	—	—
268.8	129	269.6	325	270.1	573

Absorption spectral data have been reported by JAFFÉ *et al.*[8] The wavelengths at peak absorptions agree well with the present work but the molar absorptivities do not. In the present work the three species have been clearly separated by means of the pH-absorbance study to eliminate error due to the presence of more than one species.

Solubility and solubility product of thorium-benzenephosphonate 3-hydrate

Solubilities were observed by spectrophotometric comparison of saturated solutions of thorium-benzenephosphonate 3-hydrate with synthetic standard solutions. The standard series of solutions were prepared at pH values 0.5, 1.0 and 1.5 by diluting $0.000900 M$ benzenephosphonic acid with perchloric acid solutions of pH 0.5, 1.0 and 1.5 respectively and ionic strength 1.0, adjusted by addition of sodium perchlorate. Appropriate volumes of $0.000457 M$ thorium nitrate were added last. The concentration range covered was $1.80 \cdot 10^{-6}$ to $9.00 \cdot 10^{-6} M$ thorium-benzenephosphonate. One calibration curve was drawn from the absorbances observed at 263.0 mμ since the data at the three pH values were not distinguishable from each other. The fact that these data were not distinguishable indicates that something other than the species $C_6H_5PO_3^{-2}$, $C_6H_5PO_3H^-$ or $C_6H_5PO_3H_2$ predominates, probably a soluble thorium complex.

Saturated solutions of thorium-benzenephosphonate 3-hydrate were prepared by two methods: (1) Excess thorium-benzenephosphonate 3-hydrate was shaken periodically with perchloric acid-sodium perchlorate solutions of ionic strength one, and varying pH values from 0.48 to 1.96. (2) Excess thorium-benzenephosphonate 3-hydrate was heated to about 80° C with acid perchlorate solutions of ionic strength one for about eight hours, then allowed to equilibrate at room temperature for about a week.

The spectra were observed in 10 cm silica cells with a Cary recording spectrophotometer and the absorbances at 263.0 mμ were measured. Table XIII summarizes the solubility data. A solubility product was calculated from the simplified equation, $K_{\mathrm{sp}} = (\mathrm{Th}^{+4})(C_6H_5PO_3^{-2})^2$, assuming (Th^{+4}) and $(C_6H_5PO_3^{-2})/2$ to be equivalent to the observed solubility.

The solubility product values calculated (Table XIII) agree quite well considering the fact that errors in the measured concentrations are cubed in the solubility product and that the possible presence of soluble thorium complexes was not taken into account.

TABLE XIII

SOLUBILITY AND SOLUBILITY PRODUCT OF THORIUM-BENZENEPHOSPHONATE 3-HYDRATE

pH	Absorbance	Solubility, (s), (moles $Th(C_6H_5PO_3)_2$ per liter) $\times 10^6$	Solubility product $4s^3 \times 10^{31}$
0.48	1.54	1.07	5.41
0.52	1.40	0.96	5.38
0.52	1.40	0.96	5.38
0.96	0.45	0.24	2.12
0.99	0.35	0.16	0.77
1.03	0.32	0.14	0.68
1.55	0.23	0.07	1.91
1.96	0.20	0.04	4.24
		Average	3.24

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SUMMARY

Benzenephosphonic acid quantitatively precipitates thorium as $Th(C_6H_5PO_3)_2 \cdot 3H_2O$ at pH values as low as 0.5. The compound may be dried at 140° to 180° C and weighed, as a gravimetric means of determining thorium. On ignition, $Th(C_6H_5PO_3)_2 \cdot 3H_2O$ undergoes decomposition at 240° to 300° C to form $Th(C_6H_5PO_3)_2 \cdot 2H_2O$, at 450° to 650° C to form $Th(HPO_4)_2 \cdot 2H_2O$ and finally at 800° to 1000° C to form $Th(HPO_4)_2$. The latter compound is stable to 1200° C.

Potentiometrically ($pK_1' = 0.91$, $pK_2' = 6.41$) and spectrophotometrically ($pK_1' = 0.96$, $pK_2' = 6.51$) determined pK' values are reported. Absorption spectra of $C_6H_5PO_3H_2$, $C_6H_5PO_3H^-$ and $C_6H_5PO_3^{-2}$ are reported. The solubility of $Th(C_6H_5PO_3)_2 \cdot 3H_2O$ was studied as a function of pH and the average value of the solubility product ($K_{sp} = 4s^3$) was found to be $3.24 \cdot 10^{-31}$.

RÉSUMÉ

L'acide benzènephosphonique précipite quantitativement le thorium comme $Th(C_6H_5PO_3)_2 \cdot 3H_2O$ à des pH supérieurs à 0.5. Ce composé peut être séché à 140°-180° C et pesé, ce qui permet un dosage gravimétrique du thorium. Par calcination $Th(C_6H_5PO_3)_2 \cdot 3H_2O$ est décomposé; à 240°-300° C, il y a formation de $Th(C_6H_5PO_3)_2 \cdot 2H_2O$; à 450-650° C, formation de $Th(HPO_4)_2 \cdot 2H_2O$ et finalement à 800-1000° C formation de $Th(HPO_4)_2$. Ce dernier composé est stable à 1200° C. Les valeurs de pK', obtenues potentiométriquement ($pK_1' = 0.91$, $pK_2' = 6.41$) et spectrophotométriquement ($pK_1' = 0.96$, $pK_2' = 6.51$), sont données, ainsi que les spectres d'absorption de $C_6H_5PO_3H_2$, $C_6H_5PO_3H^-$ et $C_6H_5PO_3^{-2}$. La solubilité de $Th(C_6H_5PO_3)_2 \cdot 3H_2O$ a été étudiée en fonction du pH. La valeur moyenne du produit de solubilité ($K_{ps} = 4s^3$) trouvé est de $3.24 \cdot 10^{-31}$.

ZUSAMMENFASSUNG

Die Benzolphosphonsäure fällt das Thorium quantitativ als $Th(C_6H_5PO_3)_2 \cdot 3H_2O$ aus, bei pH-Werten über 0.5. Diese Verbindung kann bei 140°-180° C getrocknet und dann gewogen werden, was eine gravimetrische Bestimmung von Thorium erlaubt. Durch Kalzinieren wird das $Th(C_6H_5PO_3)_2 \cdot 3H_2O$ zersetzt; bei 240°-300° C wird das $Th(C_6H_5PO_3)_2 \cdot 2H_2O$ gebildet, bei 450°-650° C, $Th(HPO_4)_2 \cdot 2H_2O$ und endlich bei 800°-1000° C, $Th(HPO_4)_2$. Diese letzte Verbindung ist bei 1200° C beständig. Die Werte von pK', welche man potentiometrisch ($pK_1' = 0.91$. $pK_2' = 6.41$) und spektrophotometrisch ($pK_1' = 0.96$, $pK_2' = 6.51$) erhalten hat, sind gegeben, sowie auch die Absorptionsspektren von $C_6H_5PO_3H_2$, $C_6H_5PO_3H^-$ und $C_6H_5PO_3^{-2}$. Die Löslichkeit von $Th(C_6H_5PO_3)_2 \cdot 3H_2O$ wurde untersucht in Funktion des pH-Wertes. Der mittlere Wert des gefundenen Löslichkeitsproduktes ($K_{LP} = 4s^3$) ist $3.24 \cdot 10^{-31}$.

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DETECTION AND SEPARATION OF METAL IONS ON PAPER IMPREGNATED WITH 4-HYDROXYBENZTHIAZOLE

by

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A comparison of the structural formulae of 8-hydroxyquinoline and 4-hydroxybenzthiazole shows that both compounds are amphoteric and contain a phenolic hydroxyl group adjacent to a basic nitrogen atom. These compounds should therefore behave in a similar manner with metal ions. It has been shown that 4-hydroxybenzthiazole, like 8-hydroxyquinoline, forms chelates with numerous metal ions[1], but that the former exhibits a more selective action probably due to the fact that 4-hydroxybenzthiazole is a stronger acid and a weaker base than 8-hydroxyquinoline[2].

GOTO[3] has described fluorescent tests for several metal ions based on chelate formation with 8-hydroxyquinoline, but these tests although quite sensitive, lack selectivity. The selective action shown by 4-hydroxybenzthiazole towards metal ions suggested the possibility of using it as a reagent in fluorescence analysis.

The migration of metal ions on paper impregnated with 8-hydroxyquinoline and other chelate forming reagents has been utilized for several metal ion separations[4,5]. It was therefore decided to investigate the possibility of separating metal ions using paper impregnated with 4-hydroxybenzthiazole as a chromatographic column.

4-hydroxybenzthiazole cannot be readily prepared; moreover the reported methods of preparation give unsatisfactory yields of the compound. Therefore it is unlikely that this reagent will find immediate use in classical analytical determinations, but is quite satisfactory for paper chromatography or for fluorescence analysis where relatively small amounts of the reagent are required.

PROCEDURE

4-Hydroxybenzthiazole was prepared by the method described by ERLENMEYER AND ÜBERWASSER[6]. The compound was recrystallized from 95% ethanol and had a melting point of 143° C. Ethanol solutions of the compound showed a pale green fluorescence and ammoniacal solutions of the compound had a faint greenish yellow fluorescence under ultra-violet light. The fluorescence of these solutions did not interfere with the fluorescence tests, at the dilutions used. The source of ultra-violet light used in this work was a high pressure mercury discharge tube of quartz, equipped with a filter which transmitted a band around 3650 Å.

1% solutions of the chlorides, acetates, nitrates or sulphates of these cations were used in the fluorescence tests: silver, lead, mercuric, bismuth, antimony, lithium, sodium, potassium, rubidium, beryllium, magnesium, ferric, cupric, zinc, cadmium, aluminium, calcium, strontium, barium, chromium, nickel, zirconyl, uranyl, thallium and thorium. The solutions used in paper chromatography were made from the chlorides or sulphates of cupric, nickel, zinc, aluminium, cobalt, cadmium and ferric ions. All these solutions contained 1 mg metal ion per ml.

Whatman No. 1 chromatographic paper was found to be suitable for the fluorescence tests as well as for paper chromatography. The paper was impregnated with a 2% ethanol solution of 4-hydroxybenzthiazole and dried. The paper was then cut into strips for paper chromatography, and to any convenient size for the fluorescence tests.

The fluorescence tests were carried out as follows: 0.01 to 0.02 ml of the cation solution was spotted on the paper by means of a micropipette, the spot exposed to ammonia vapour and then examined under ultra-violet light for fluorescence. The spot was then moistened with a drop of water, exposed to the vapour of glacial acetic acid for some time and examined again in ultra-violet light for the persistence of fluorescence. Sensitivity tests were carried out in a similar manner: standard solutions of the metal ions were made and the paper was spotted with a known volume of the standard solution by means of a micropipette, exposed to ammonia vapour and then examined under ultra-violet light. Blank fluorescence tests were carried out with the reagent and ammonia, and also with the metal ion and ammonia.

In the chromatographic work the descending technique was used. Whatman No. 1 paper impregnated with the 4-hydroxybenzthiazole was cut into strips 9 cm wide and 54 cm in length. 0.01 ml of the metal ion solution was applied to the paper, by means of a micropipette, 5 cm from the surface of the developing solvent. When mixtures of the metal ions were used, 0.02 ml of the mixture was spotted on the paper in an identical manner. The mixtures of the metal ions were made up to contain 1 mg of each metal ion per ml of the solution. The chromatograms were developed for 6 to 8 hours at room temperature using methanol or ethanol as the developing solvent. After development, the strips of paper were dried and examined in daylight and in ultra-violet light. Exposure of the chromatograms to ammonia vapour after development, facilitated the detection of the position of the metal ions.

The R_F values given in Table I are average values of four separate experiments. The R_F values for aluminium and ferric ions are reproducible to ± 0.04.

RESULTS AND DISCUSSION

Paper impregnated with 4-hydroxybenzthiazole gave with zinc, magnesium and cadmium ions in the presence of ammonia, an intense blue fluorescence when examined under ultra-violet light. Silver ions under the same conditions gave a blue green fluorescence, zirconyl ions a greenish yellow fluorescence, calcium, strontium and barium ions a pale blue fluorescence and lithium, sodium, potassium and rubidium ions a very pale blue fluorescence under ultra-violet light. None of the other cations tested gave a fluorescence under the conditions employed.

The most noteworthy difference between the fluorescence properties of the compound formed by 8-hydroxyquinoline and 4-hydroxybenzthiazole with metal ions, is that 4-hydroxybenzthiazole does not form a fluorescent compound with aluminium and beryllium ions. 8-Hydroxyquinoline however, is known to form yellow or yellowish green fluorescent chelates with aluminium, zinc, cadmium, calcium, magnesium, beryllium and zirconyl ions[3]. It is possible that some of the fluorescence effects observed with 4-hydroxybenzthiazole and metal ions may be due to surface adsorption of the type that has been described by FEIGL[7].

It was found possible to differentiate between the blue fluorescent chelates of zinc, cadmium, magnesium and silver and the fluorescent compounds obtained with lithium, sodium, potassium, rubidium, calcium, barium and strontium ions. On exposure of the moistened fluorescent spot to the vapour of glacial acetic acid, it was found that the fluorescent compounds formed by lithium, sodium, potassium, rubidium, calcium, strontium and barium, did not last for more than 10 to 15 seconds, whereas the silver, zinc, cadmium and magnesium chelates gave a blue fluorescence which persisted up to a period of about 3 minutes. The greenish yellow fluorescence given by the zirconyl ion lasted for about half a minute in the presence of acetic acid vapour.

Identical tests carried out with 8-hydroxy- quinoline impregnated paper showed that the fluorescence given by magnesium and calcium ions did not persist in the presence of acetic acid vapour for more than 30 to 45 seconds, and that given by the zinc and cadmium ions was unaffected by the acid vapours over a period of about 5 minutes.

Sensitivity tests which were carried out with zinc, cadmium and magnesium ions showed that the fluorescence tests with 4-hydroxybenzthiazole were as sensitive as those with 8-hydroxyquinoline[3]. 0.25 microgram of zinc and 0.1 microgram of cadmium could be detected by this test; but the test was sensitive to only 1.0 microgram of magnesium. As in the case of 8-hydroxyquinoline several cations mask the fluorescence of zinc, cadmium, magnesium and silver with 4-hydroxybenzthiazole, notably ferric ion which forms bluish green complex with 4-hydroxybenzthiazole.

The R_F values obtained with methanol are almost identical to those obtained with ethanol as the developing solvent. All the metal ions except aluminium and ferric ions showed a considerable amount of tailing and consequently the R_F values for zinc, cadmium, copper, nickel and cobalt ions are of little significance.

Since only the ferric and aluminium ions migrated to any appreciable extent, it should be possible to separate either of these ions from zinc, cadmium, copper, nickel and cobalt. Mixtures containing aluminium together with each of the metal ions, zinc, cadmium, copper, nickel and cobalt, were prepared. These mixtures were chromatographed on 4-hydroxybenzthiazole impregnated paper and it was found that in every case a definite separation was obtained, using either methanol or ethanol as the developing solvent. In these separations the R_F value of the aluminium was unaltered, but the R_F values of the zinc, cadmium, copper, nickel and cobalt ions were somewhat lower than those given in Table I.

TABLE I

R_F VALUES OF CATIONS ON PAPER IMPREGNATED WITH 4-HYDROXYBENZTHIAZOLE

Cation	Developing Solvent	
	Methanol	Ethanol
Fe^{+3}	0.59	0.57
Al^{+3}	0.65	0.66
Zn^{+2}	0.10	0.15
Cd^{+2}	0.22	0.23
Cu^{+2}	0.25	0.21
Ni^{+2}	0.15	0.16
Co^{+2}	0.25	0.20

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SUMMARY

Zinc, magnesium and cadmium ions in the presence of ammonia, form intense blue chelates on paper impregnated, with 4-hydroxybenzthiazole. 0.25 microgram, 1.0 microgram and 0.1 microgram respectively, of these metal ions can be detected by means of this test. Several cations interfere.

Alumunium can be separated from zinc, cadmium, copper, nickel and cobalt on paper impregnated with 4-hydroxybenzthiazole, which acts as a chromatographic column.

RESUME

Le zinc, le magnésium et le cadmium donnent, en présence d'ammoniaque, des chélates bleu intense sur des papiers imprégnés de 4-hydroxybenzthiazole. Cette réaction permet de déceler respectivement 0.25 µg, 1.0 µg et 0.1 µg de ces ions métalliques. Plusieurs cations gênent. L'aluminium peut être séparé du zinc, du cadmium, du cuivre, du nickel et du cobalt, sur papier imprégné de 4-hydroxybenzthiazole, agissant comme colonne chromatographique.

ZUSAMMENFASSUNG

Das Zink, das Magnesium und das Cadmium geben, in Anwesenheit von Ammoniak, intensiv blaue Chelate, auf mit 4-Hydroxybenzthiazol imprägniertem Papier. Diese Reaktion erlaubt 0.25 µg, 1.0 µg und 0.1 µg respektiv, dieser Metallionen zu bestimmen. Mehrere Kationen stören. Das Aluminium kann getrennt werden von Zink, Cadmium, Kupfer, Nickel und Kobalt auf Papier, das mit 4-Hydroxybenzthiazol imprägniert ist, welches als chromatographische Kolonne wirkt.

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THE ROLE OF COMPLEX FORMATION IN PARTITION PAPER CHROMATOGRAPHY

by

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In an earlier paper[1] information on the role of chemical reaction in differential ionic movement was obtained by using alcoholic KCN as the solvent. Many inorganic cations reacted to form both a sparsely soluble metal cyanide and a soluble cyanide complex. An examination of chromatograms developed with this solvent indicated that variation of either the concentration of cyanide in the solvent or the concentration of inorganic cation in the "spot" resulted in widely differing R_F values. The area of the developed spot also varied with different ratios of the two reactants. Other workers[2,3] who studied amino acids, found that unless the pH of the solvent was carefully controlled, reproduceable R_F values and spot areas could not be obtained.

In view of the use made of chromatograms for qualitative analysis and for quantitative estimations based on the measurement of spot areas, or photometric methods using maximum colour density[4-9], it was felt that further information on the effect of reaction between solvent and solute would be of considerable interest.

As a preliminary to other investigations, a study was made of the movement of various cations in paper chromatograms developed with solvents containing varying amounts of disodium ethylenediaminetetraacetate. Salts of this organic acid (E.D.T.A.) are renowned for the number and stability of the complexes they form with the alkaline earths and heavy metals. However, as neither these salts nor the metal complexes are soluble in organic solvents and exhibit only limited solubility in aqueous alcoholic solutions, the choice of a solvent was rather restricted. A mixture of equal volumes of aqueous complexing agent and absolute alcohol was finally chosen.

PROCEDURE

Equal volumes of standard solutions of the inorganic cations Ag^+, Pb^{+2}, Hg^{+2}, Cu^{+2}, Cd^{+2}, Bi^{+3}, Fe^{+2}, Fe^{+3}, Cr^{+3}, Mn^{+2}, Zn^{+2}, Ni^{+2}, Co^{+2}, Ti^{+4} and Mg^{+2} were "spotted" in similar positions on a series of rectangular paper strips prepared from Whatman No. 1 Filter Paper. These papers were suspended in enclosed glass vessels with the lower end dipping into the alcoholic solvent which contained concentrations of disodium ethylenediaminetetraacetate varying from $10^{-2}N$ to $10^{-4}N$. After a standard period of development the papers were removed and the new positions of the cations located by exposure to H_2S or treatment with some other suitable reagent. These chromatograms were then repeated using solvents which were approximately decinormal in respect to either H_2SO_4 or NH_4OH. Fig. 1 illustrates the nature of the chromatograms so obtained.

The R_F value and the approximate area of each of these spots were then determined and plotted against the concentration of complexing agent in the solvent. A series of the resulting curves is shown in Figs. 2-9.

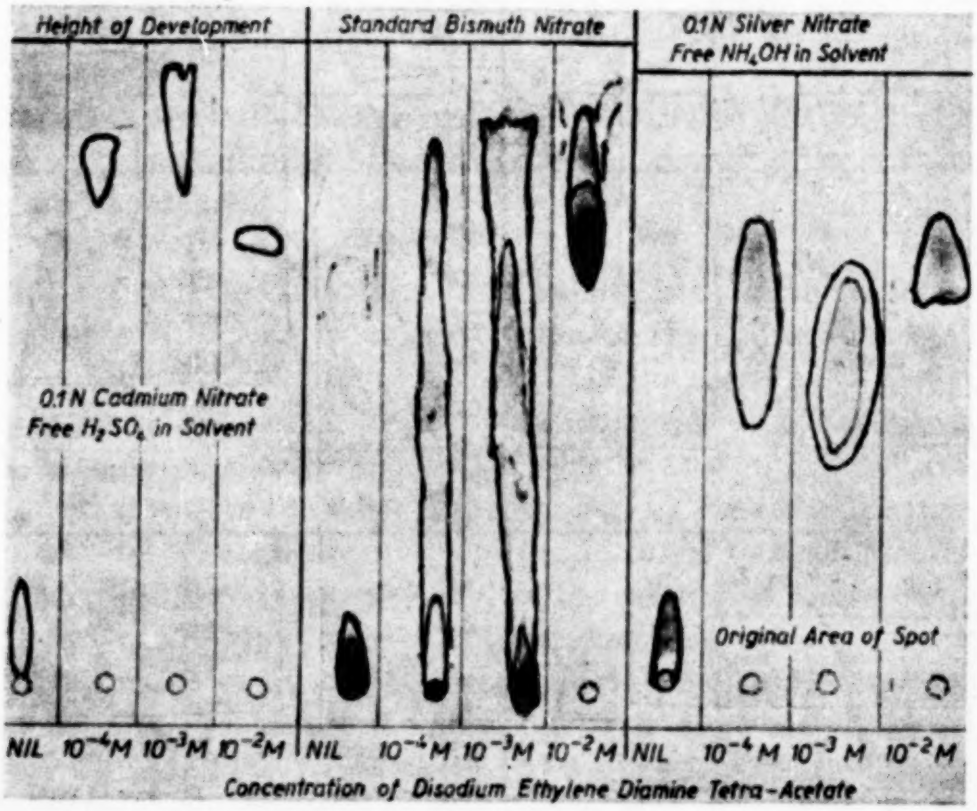
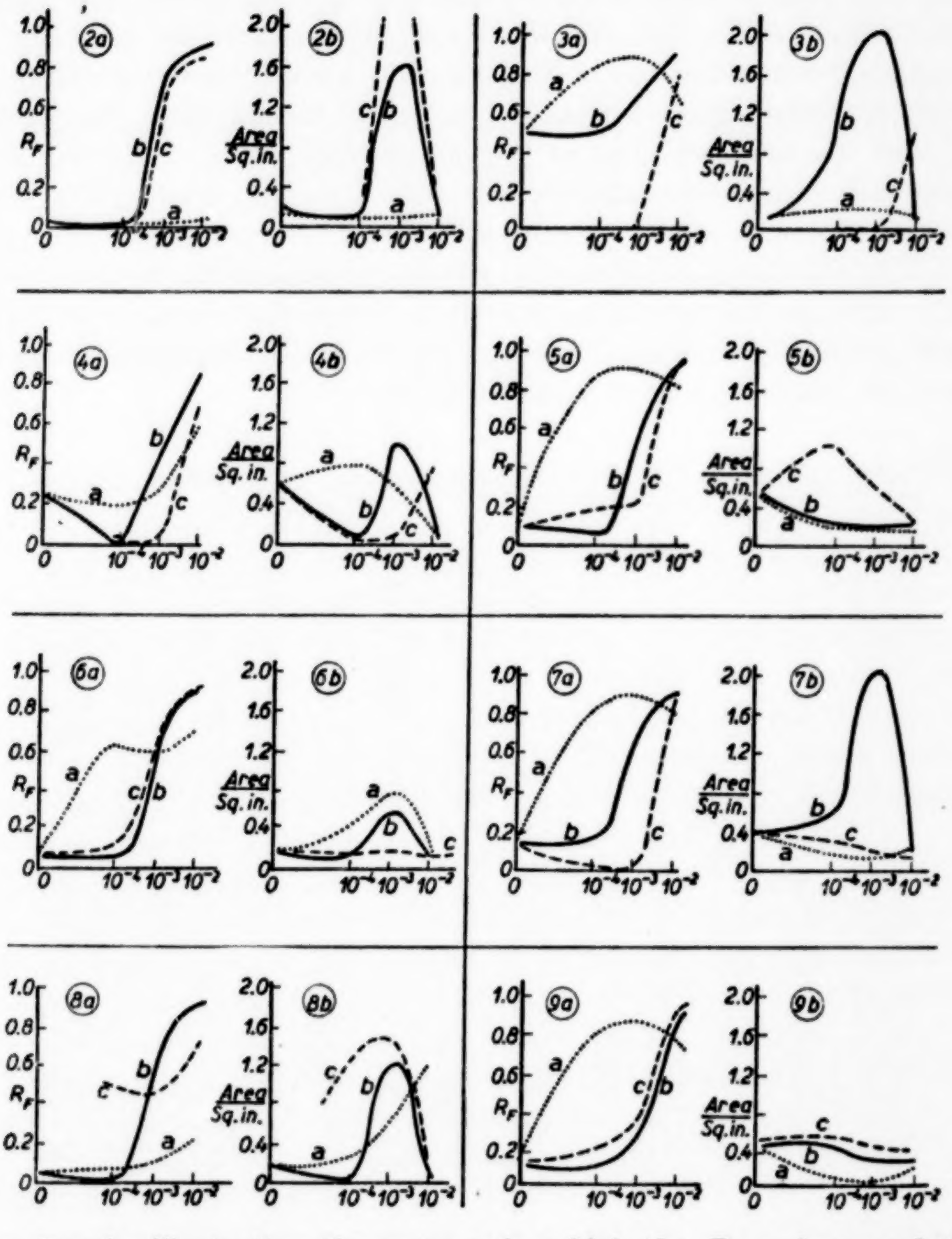

Height of Development
Standard Bismuth Nitrate
0.1N Silver Nitrate
Free NH₄OH in Solvent
0.1N Cadmium Nitrate
Free H₂SO₄ in Solvent
Original Area of Spot
NIL 10⁻⁴M 10⁻³M 10⁻²M
NIL 10⁻⁴M 10⁻³M 10⁻²M
NIL 10⁻⁴M 10⁻³M 10⁻²M
Concentration of Disodium Ethylene Diamine Tetra-Acetate

Fig. 1. Typical chromatograms illustrating the manner in which the area of spots varied with changing concentrations of E.D.T.A. in the solvent.

DISCUSSION

The development of a chromatogram has been visualised as follows. During the rise of the solvent (by capillary action) through the zone of the solute, either whole or partial saturation may occur and the dissolved solute will tend to pass out of solution again at a rate dependent on the relative partitional distribution which exists between the solvent and the non-mobile phase. The greater the



Figs. 2-9. Graphs illustrating the manner in which the R_F values and the area of spots of many inorganic cations varied with changing concentrations of E.D.T.A. in the solvent (b) and the presence of free acid (a) or ammonia in the solvent (c).

2 0.1 N lead nitrate
3 0.1 N ferric nitrate
4 Standard mercuric chloride
5 0.1 N nickel nitrate
6 0.1 N copper nitrate
7 0.1 N cobalt nitrate
8 0.1 N silver nitrate
9 Standard zinc nitrate

2a, 3a, *etc*. Variation in R_F value
2b, 3b, *etc*. Variation in spot area
Abscissae in all cases: molarity of E.D.T.A.

solubility of the ion in the solvent, the further it is transported along the paper by a given volume of the solvent[10].

When chemical reaction occurs between solvent and solute, the solubilities of the solute and reaction products may vary greatly. The nature and extent of the reactions will be controlled to a large degree by the relative proportions of the two reactants, although diverse ions present may affect the equilibrium.

The results obtained in this investigation confirm these views. The graphs in Fig. 1 illustrate the manner in which R_F values and spot areas varied with changing concentrations of complexing agent and the presence of free acid or free base in the solvent. The stability of some complexes made identification difficult at times, but results given are typical of the trends in all cases.

Using aqueous alcohol as the solvent, the appreciable solubility of many solutes caused the cations to diffuse upwards in the solvent yielding marked R_F values and increased spot areas.

The addition of small amounts of disodium ethylenediaminetetraacetate to the solvent was sufficient to convert some of the solute to a stable complex possessing a different solubility and distribution coefficient. The reaction was indicated by increased tailing of the spots, and at a critical concentration many examples were noted where the cations were located in diffuse areas extending from the original spot to the wave front (*cf.* Fig. 2). By assuming that the volume of solvent passing through the spot was proportional to the diameter of the spot times the height of development and that the volume of solute was proportional to the area of the spot, it was calculated that this critical concentration was that which provided one mole of complexing agent per mole of solute. This is in agreement with the accepted knowledge that most metals form 1 : 1 molar complexes with E.D.T.A. With a solvent of this dilution, small amounts of the solute would be slowly but continually taken into solution as the complex and this mode of reaction during development would explain the large spots obtained.

With higher concentrations of active agent in the solvent, conversion of the solute to the complex was more rapid and the soluble complexes were able to move with the aqueous wave front resulting in higher R_F values and less diffuse spots. Unfortunately, due to the limited solubility of the complexing agent, solutions more concentrated than $10^{-2}M$ could not be prepared.

In acid solutions, spot areas varied little but the R_F values were generally high even in the presence of small amounts of E.D.T.A. This could be due to the continuous formation of an unstable complex which possesses high solubility.

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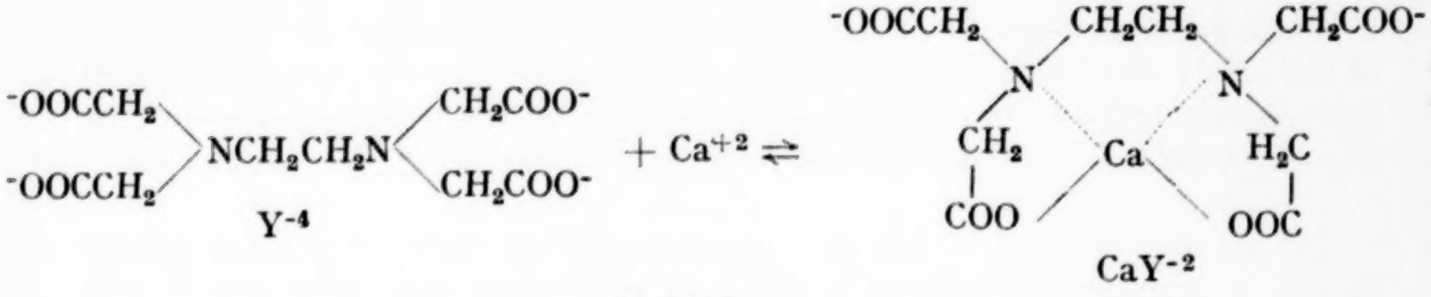
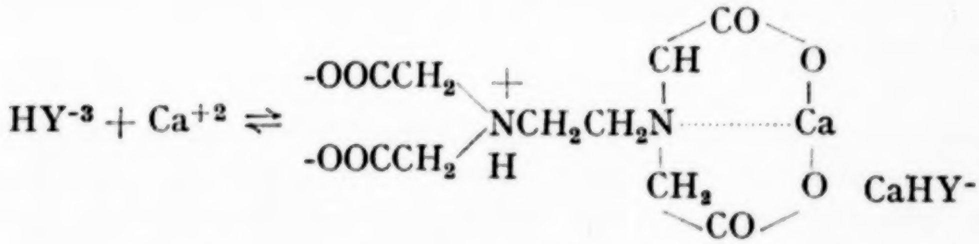
The reactions which occur between E.D.T.A. and calcium (other metals behave similarly) have been described as follows[11]: In alkaline solution



$^{-}OOCCH_2$
$^{-}OOCCH_2$
NCH_2CH_2N
CH_2COO^{-}
CH_2COO^{-}
Y^{-4}
$+ Ca^{+2} \rightleftharpoons$
$^{-}OOCCH_2$
CH_2CH_2
CH_2COO^{-}
N
N
CH_2
Ca
H_2C
COO
OOC
CaY^{-2}

$$\text{and } K_2 = \frac{[CaY^{-2}]}{[Ca^{+2}]\ \ [Y^{-4}]} = 3.9 \times 10^{10}; \qquad \text{(A)}$$

At lower pHs, a second complex is formed but to a limited extent only;



$HY^{-3} + Ca^{+2} \rightleftharpoons$
$-OOCCH_2$
$-OOCCH_2$
+
NCH_2CH_2N
H
CO
CH
O
Ca
CH_2
O
CO
$CaHY^{-}$

$$\text{and } K_1 = \frac{[CaHY^{-}]}{[Ca^{+2}]\ [HY^{-3}]} = 3200 \qquad \text{(B)}$$

The reactions in the acidic solvent would favour the formation of this latter complex when the equilibrium conditions (*cf.* Equation B) were satisfied. Decomposition of the complex can therefore be expected to occur when the solvent passes out of the zone of high cation concentration. The continuous process of complex formation, movement of the complex to the edge of the spot and the subsequent decomposition could explain the consistently small spot areas and the general increase in R_F values with increasing concentrations of E.D.T.A., the latter factor tending to increase the stability of the complexes. The only exceptions noted to the general trend of high R_F values were the movements of the cations Ag^{+}, Pb^{+2}, Hg^{+2} and Bi^{+3}.

The underlying reactions in the ammoniacal solutions are more complex as the ammonia itself is capable of forming sparsely soluble compounds with most of the cations examined and soluble ammine complexes with many. These reactions themselves result in differential movement. The slightly soluble salts formed by the ammonia would be soluble in ethylenediaminetetraacetate solutions in accordance with the following theory[12].

For the reaction $MX + Y^{-4} = MY^{-2} + X^{-2}$ where MX is the poorly soluble

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salt and MY^{-2} the soluble E.D.T.A. complex, the equilibrium constant $K_s = \frac{(MY^{-2})\,(X^{-2})}{(MX)\,(Y^{-4})}$ and $K_s = (K_2) \times (K_{sp})$ where K_2 is the stability constant of the MY^{-2} complex and K_{sp} is the solubility product of the salt MX.

If K_s is much larger than unity then the salt MX will dissolve completely, if it is less than one, the solubility of MX in the E.D.T.A. solution will decrease accordingly. As a result of these competing equilibria, it was found that marked increase in R_F values generally occurred only when the strength of the E.D.T.A. was comparable with the concentration of ammonia present. However, those cations capable of forming stable complexes with ammonia (*e.g.* Ag^+, Cu^{+2}, Cd^{+2}, Ni^{+2}) showed marked R_F values even in the presence of very little E.D.T.A.

Although there were some exceptions to the above generalizations due to individual characteristics of the cations concerned, the evidence is conclusive that chemical reaction between solvent and solute can play a major role in differential ionic movement. Thus in qualitative or quantitative analyses based on the measurement of R_F values or spot areas, it is essential to standardize all conditions which may affect any possible chemical equilibria. Failure to observe these precautions can only lead to false or inaccurate conclusions.

CONCLUSIONS

This investigation confirmed an earlier belief that chemical reaction between solvent and solute can markedly affect the behaviour of the solute during the the development of a chromatogram. Any variations in those conditions which alter the equilibrium of such chemical reaction can influence the resulting R_F value and spot area.

It is therefore important in all partition paper chromatographic studies to consider the possibility of chemical interaction during development, and if reaction is anticipated, great care should be taken in controlling conditions and interpreting results.

SUMMARY

Further information of the possible effects of chemical reaction on differential ionic movement in partition paper chromatography was obtained by developing chromatograms of fifteen inorganic cations with alcoholic solvents containing varying concentrations of disodium ethylenediaminetetraacetate.

An examination of these chromatograms indicated that variations in the concentrations of E.D.T.A. in the solvent or the presence of free acid or ammonia resulted in marked changes in R_F values and spot areas.

It is therefore suggested that care should be taken in interpreting the results of any chromatograms developed with solvents capable of chemical interaction with the "spotted" solute.

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RÉSUMÉ

On a pu obtenir des renseignements supplémentaires au sujet des effets possibles des réactions chimiques sur les mouvements ioniques différentiels en chromatographie sur papier; pour cela on développe les chromatogrammes de 15 cations inorganiques à l'aide de solutions alcooliques contenant des concentrations variables de sel de sodium de l'acide éthylènediaminotétraacétique.

En étudiant ces chromatogrammes, on a constaté que les différents degrés de concentration de EDTA dans les solutions, ou la présence d'acide libre ou d'ammoniaque, causent des variations considérables du R_F et des surfaces tachées. On doit donc faire bien attention en interprétant les chromatogrammes obtenus à l'aide de solvants pouvant réagir chimiquement avec la tache formée.

ZUSAMMENFASSUNG

Die Entwicklung der Chromatogramme von fünfzehn anorganischen Kationen mit alkoholischen Lösungen, die verschiedene Konzentrationen von Dinatriumethylendiamintetraazetat enthalten, gab weitere Auskunft bezüglich der möglichen Wirkung chemischer Reaktionen auf die Ionenbewegung in der Papierchromatographie.

Eine Untersuchung dieser Chromatogramme zeigte an, dass Änderungen in der Konzentration von E.D.T.A. in der Lösung oder die Anwesenheit von freier Säure oder Ammon beträchtliche Änderungen der R_F-Werte und der Tüpfelflächen verursachen.

Es scheint daher angebracht, bei der Auslegung der Ergebnisse eines jeden Chromatogramms, das mit Lösungsmitteln entwickelt wurde, die chemische Reaktionsfähigkeit mit der „Tüpfellösung" besitzen, äusserste Sorgfalt anzuwenden.

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QUANTITATIVE INORGANIC PAPER CHROMATOGRAPHY DIRECT DETERMINATION OF COBALT BY A SCANNING METHOD

by

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INTRODUCTION

In earlier publications[1,2] we have described a method for the direct determination of inorganic ions on filter paper, after previous elimination of interfering ions by paper chromatography. Reflectance spectrophotometry was used for measuring the specific colour intensity of the spots produced by spraying with a suitable reagent solution. Although this method is very accurate, it is applicable only if the R_F value of the ion to be determined is zero or very low while that of the interfering ions is high. We found that for nickel these conditions could generally be fulfilled. However, this may not always be possible for other ions. In such cases the direct quantitative determination of spots which move for varying distances with the solvent mixture can be accomplished only by the use of a scanning technique. Although these methods are widely used for the determination of organic substances[3,4,5,6,7,8,9,10,11] they have not as yet been applied in inorganic analysis and it is generally believed that their accuracy is rather poor. Accordingly, the present investigation was undertaken to find out what degree of accuracy can be expected from a scanning method applied to inorganic paper chromatography.

The separation and determination of cobalt was selected for detailed study.

DEVELOPMENT OF THE METHOD

The techniques used for chromatography and colour production were essentially those already described[1,2]. For colour measurement, a Beckman DU spectrophotometer and a Photovolt Electronic Densitometer Mod. 525 were available. The latter instrument was equipped for transmission measurements only. The Beckman spectrophotometer could be used for transmission and reflectance photometry. However, a rather large surface is needed for accurate reflectance measurements, and consequently disproportionately large chromatograms would have been needed. Moreover, the reflectance attachment of the Beckman spectrophotometer is not easily adaptable to continuous scanning. In view of this it was decided to use transmission measurements only.

(a) *Production of initial spots*

Whatman No. 1 paper, which was used in our previous experiments proved satisfactory again. It contains no measurable amounts of nickel and cobalt and only slight traces of copper. It is not as uniform with respect to light transmission as might be desired, but no other paper could be found with a higher degree of uniformity.

For the initial solution $3N$ hydrochloric acid was used; we have shown that this gives very uniform initial spots. When using a scanning method it is of course necessary to apply identical volumes of solution (both standard and unknown) on the filter paper. These volumes must be such that the resulting spots are as small as possible, yet larger than the area illuminated during colour measurement. In our case this latter area measured 3 mm × 10 mm for the Beckman instrument (dimensions of the light beam at a distance of 1 cm from the exit window) while for the Photovolt densitometer a 1 mm × 15 mm slit was selected; spots about 15 mm in diameter, corresponding to an initial volume of 10 μl were found to be convenient. This volume is applied on the paper by means of a very accurate micropipette. Standards and unknowns are applied on the same paper sheet and at the same time, and are allowed to dry at room temperature without any ventilation. In this way a series of uniform initial spots is obtained.

(b) *Chromatography*

The ascending chromatography described previously for the determination of nickel[1,2] was used. On paper squares measuring 23 cm × 23 cm at least eight spots can be placed (*e.g.* four standards, four unknowns).

The developing solvent (acetone, 90 ml; HCl (25 %) 10 ml; acetylacetone, 2 ml) produces complete separation of cobalt from nickel and copper (which give coloured compounds with the spraying reagent) and all other common elements.

It can be used when the cobalt content of the initial solution is less than 8 mg/100 ml. However the spots are rather too compact and the following solvent was found to be more convenient: *n*-butanol, 30 ml; acetone, 56 ml; HCl (25 %) 12 ml; acetylacetone, 2 ml (Fig. 1). The initial solution should not contain more than 20 mg Co/100 ml.

Separation of cobalt from the other metals is complete, without lateral spreading of the spots, and consequently without danger of interference from adjacent spots of the same metal. This obviates the necessity for the use of a constricted channel such as described by MÜLLER AND CLEGG[12]. The technique we employed is also superior to chromatography on narrow strips, because spots of the standards

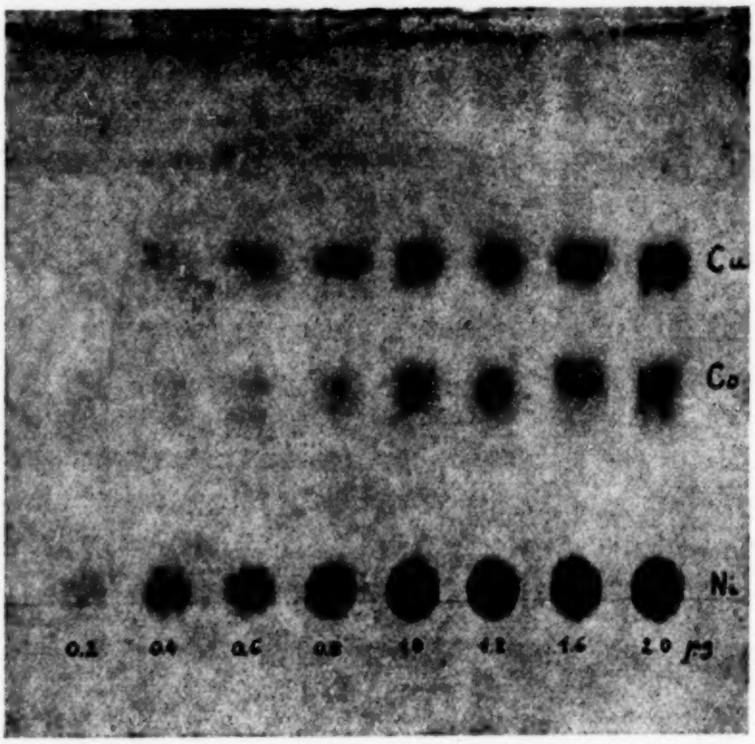

Fig. 1. Chromatogram of spots containing 0.2—2 µg Ni, Co and Cu in equal amounts.

and unknowns can be developed side by side on the same paper and under exactly the same conditions.

We also observed that in order to obtain reproducible results, the moisture content of the filter paper should be controlled. This was already pointed out by REDFIELD AND GUZMAN[13]. Accordingly all operations were at first carried out in a conditioned room in which the relative humidity of the air was maintained at 65 % and the temperature at 20° C. Identical results could be obtained by conditioning the paper cylinders for one hour in a small constant-humidity cabinet. A relative humidity of 65 ° was easily maintained by placing a tray containing a saturated ammonium nitrate solution in the air stream of an electric fan. The cylinders were transferred as rapidly as possible from this cabinet to the chromatography jars.

If another level of air humidity is chosen, the composition of the eluting solvents may have to be changed, in order to obtain optimal results.

Later it was observed that when large quantities of iron are present, as for the determination of cobalt in alloy steels, high results are obtained. This appears to be due to a narrowing of the cobalt spot. In this case conditioning for at least 6 hours in an atmosphere saturated with the developing solvent prior to chromatography causes diffusion of the iron, and accurate results can then be obtained.

R_F values are similar to those given previously[1,2].

It takes about two hours for the dry solvent front to reach the top of the paper cylinder. However, in order to obtain optimal resolution, the paper is left in the

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jar for at least another half-hour, during which time the wet solvent front continues to advance slowly. It is even permissible to start the development in the evening and leave it going on overnight; no excessive diffusion of the spots results.

The same solvent can be used for several runs; after three days it is discarded.

(c) *Colour production*

Rubeanic acid (dithio-oxamide) gives coloured compounds with nickel (blue) cobalt (yellow) and copper (green).

A 0.03 % solution in ethanol containing 5 % conc. ammonia solution, is sprayed evenly on both sides of the chromatogram as described previously[2]. The spraying reagent is not stable and should be prepared immediately before use. Quantities as low as 0.1 μg of either nickel, cobalt, or copper are revealed as distinctly visible spots, the colour of which appears indefinitely stable when protected from daylight.

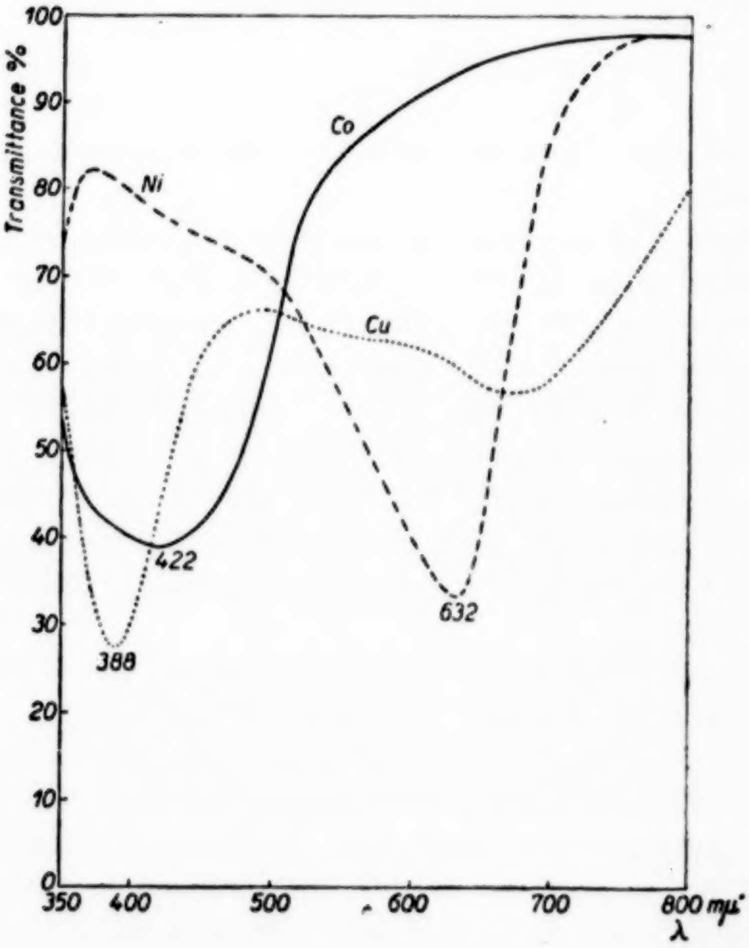

Fig. 2. Transmission curves of spots containing equal amounts of Ni, Co and Cu (values corresponding to the area of minimum transmittance).

The spectral transmission curves of spots containing equal amounts of Ni, Co and Cu were determined on the Beckman DU instrument, a blank paper being used as the 100 % transmission standard (Fig. 2). The absorption maximum is at 632 mμ for Ni, at 422 mμ for Co and at 388 mμ for Cu.

(d) *Colour measurement*

(1) *Principle.* The paper sheet is cut into strips parallel to the direction of solvent flow. Each strip is scanned at definite intervals along the length of the chromatogram using light of a wavelength giving maximum absorption with the coloured spot. In this way curves of absorbance versus distance are obtained. The best apparent base line is drawn and either the height or the area of each peak is determined. As there is a nearly linear relation between these quantities and concentration, a calibration curve can be drawn using the values found for the standards. The unknown concentrations are calculated from these curves.

(2) *Apparatus.* The Photovolt Densitometer Model 525 is especially designed for scanning paper chromatograms. It has a high sensivity and narrow-band filters can be used.

For the Beckman DU spectrophotometer a special adapter was constructed (Fig. 3). This apparatus replaces the absorption cell compartment, which is removed. It consists of a frame supporting two pairs of rubber-covered spindles. These are in close contact, which prevents slipping of the paper. The pair of spind-

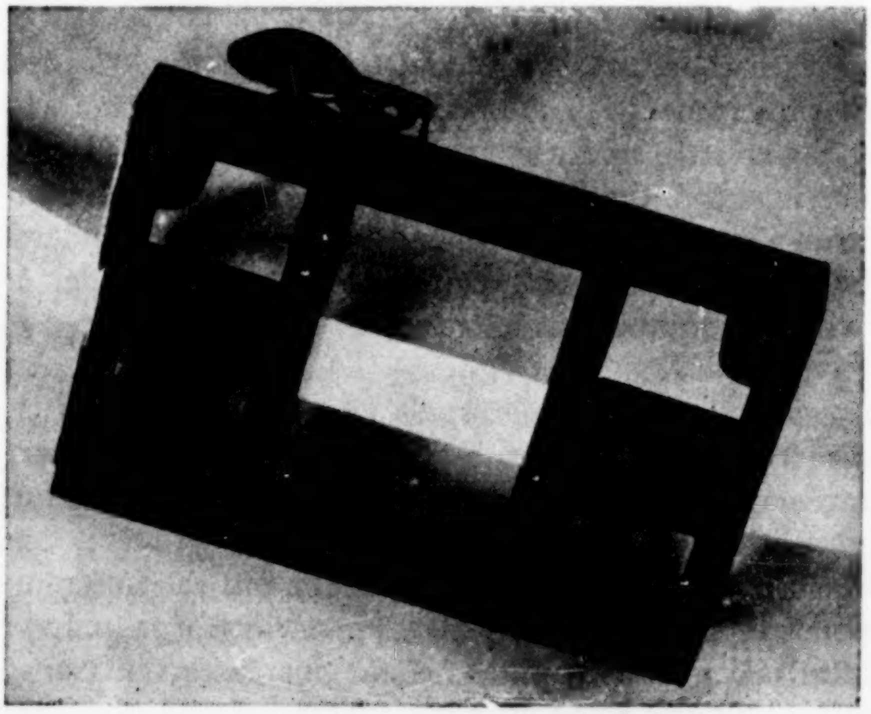

Fig. 3. Adapter for paper strips.

les nearest the lamp-holder can be made to rotate for an accurately known amount by means of a graduated knob and a gearing mechanism. The paper strip, 20 mm wide, enters through a slit measuring 20 mm × 2 mm, passes between the spindles and leaves the adapter through another slit. Guides prevent any lateral displacement. By turning the graduated knob the paper is made to advance; one division corresponds to 1 mm.

(3) *Procedure.* We operated as follows. After chromatography the paper sheet (with eight original spots) is cut into eight strips 20 mm wide. Each strip contains a complete chromatogram and it is cut in such a way that all the spots are well centred. For use with the Beckman instrument the strips are attached end to end by means of adhesive tape so that a long film is obtained. This is positioned in the adapter in such a way that the light beam crosses a portion of blank paper just in front of the first cobalt spot. Care should be exercised to guide the strip through the exit slit, and it is best to attach a blank strip in front of the film. The adapter is then put in place and the wavelength dial is set at the absorption maximum of the cobalt (422 mμ). The density knob is set at zero (100 % transmission) and the instrument brought to balance in the usual way, a minimum slit width being used. The paper film is advanced 2 mm by turning the graduated knob, the spectrophotometer is adjusted with the density knob and the reading is recorded. Another movement of the paper is then made, the spectrophotometer is adjusted again, and the second reading is recorded. This process is continued until the entire spot has been scanned.

When the first Co spot has completely crossed the light beam, the procedure is renewed for the following spot.

Measurement with the Photovolt Model 525 is slightly less precise but much more rapid. This instrument is equipped with a scanning stage which transports both the filter paper strip and a chart paper. The strip is placed between two transparent plastic strips, the lower of which has a groove 20 mm wide, so that the paper strip is always held in the same position. The standard incandescent lamp is used with a slit aperture 1 mm wide and 15 mm long. A narrow-band gelatin filter with maximum transmittance at 420 mμ is placed in front of the search unit.

The strip is scanned at 1 mm intervals and the readings of the photometer are recorded directly on chart paper so that a complete density curve is obtained.

The transparency of Whatman No. 1 paper is sufficient for transmission measurements. With the Beckman spectrophotometer zero density readings could be obtained from 375 mμ upwards. At 422 mμ the minimum slit width is about 0.55 mm, corresponding to an effective band width of 7 mμ. Impregnation with paraffin, paraffin oil, α-bromonaphtalene, *etc.*, increases the transparency about twofold, but it is tedious and also increases the irregularity of the paper. Whatman No. 1 paper impregnated with paraffin oil allows readings down to 350 mμ.

The Photovolt instrument is also sufficiently sensitive to permit the use of non-impregnated filter paper.

No filter paper is quite satisfactory with respect to uniformity. Different types and grades were examined but none proved outstandingly superior. This is the principal factor limiting the precision of the method.

Typical absorbance curves obtained with the Beckman spectrophotometer are given in Fig. 4. With the Photovolt densitometer similar curves are obtained, but the peaks are slightly lower.

A similar method can be used for the determination of nickel and copper, but this was not further investigated.

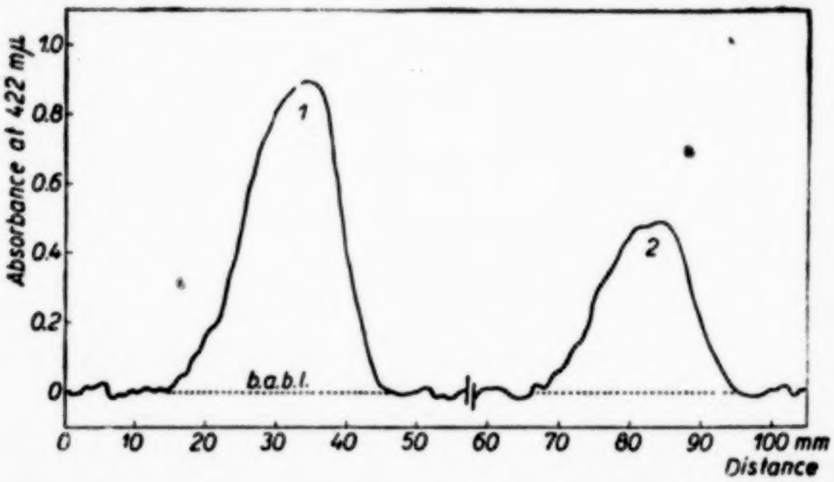

Fig. 4. Absorbance curves obtained with (1) 2 μg Co; (2) 0.8 μg Co (b.a.b.l. = best apparent base line).

PRECISION AND ACCURACY

Precision. The coefficient of variation of a single measurement relative to the mean on the same chromatogram was determined in the following way. A series of 6 chromatograms was prepared, each containing eight identical spots.

The cobalt concentrations used were 20, 16, 12, 8, 4 and 2 mg Co/100 ml 3*N* HCl, so that the spots of each chromatogram contained resp. 2, 1.6, 1.2, 0.8, 0.4 and 0.2 μg Co. After chromatography and colour development the spots were scanned in the usual way and the absorbance curves plotted on chart paper. The best apparent base line was drawn for each spot and its height (maximum absorbance) as well as the total enclosed area were calculated. It was found that for the range 20-4 mg Co/100 ml the coefficient of variation of a single measurement is about 7 % for the height and 6.5 % for the enclosed area, irrespective of concentration. Below 4 mg Co/100 ml the coefficient of variation rises steeply to about 10 % at 2 mg Co/100 ml. At first sight it would appear that both measurements are nearly equivalent, and as the height (maximum absorbance) is much more easily obtained than the enclosed area, determination of the latter would appear superfluous. However, the average calibration curve for the area is nearer a straight line than the curve for the height (Fig. 5) so that the coefficient of variation of a single measurement expressed in % Co, increases from 7 to 10 % (from 4 to 20 mg Co/100 ml) when using the height, and only from 6.5 to 7.5 % when using the total area. Also the graphs for the height differ much more from one chromatogram to another than the graphs for the area.

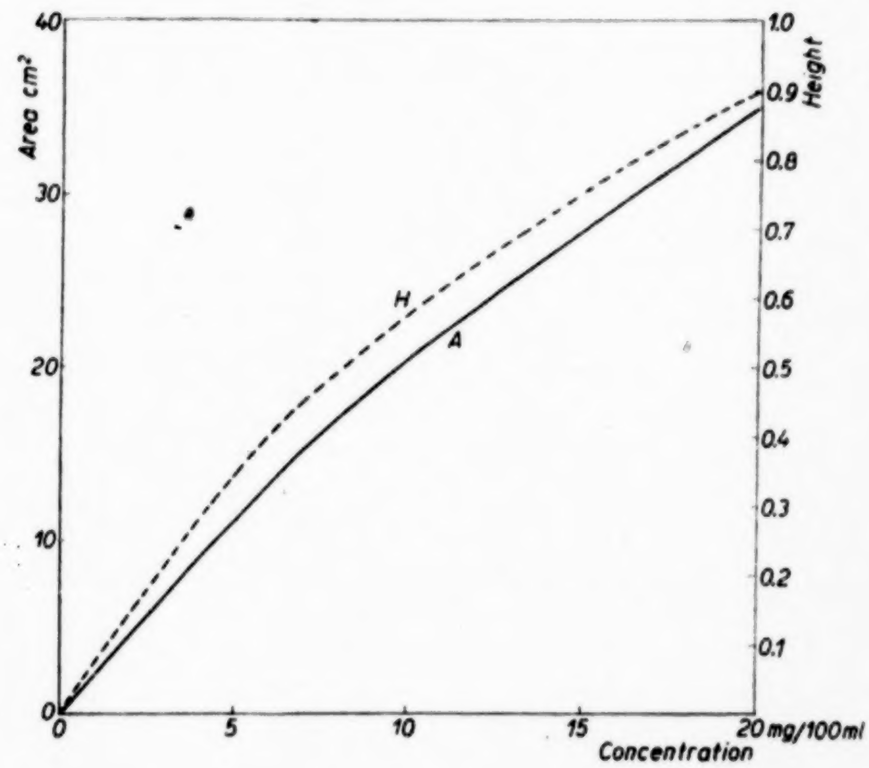

Fig. 5. Calibration graphs, corresponding to the average absorbance curves obtained from spots containing 0—2 μg Co.
H = height (maximum absorbance)
A = enclosed area

Theoretically the coefficient of variation between the means obtained for an unknown on chromatograms each containing 4 (different) standards and 4 unknowns (either identical or at different dilutions) using the most probable graph corresponding to the standards, would be about equal to the coefficient of variation of a single measurement. This was borne out in practice, the coefficient of variation computed from nearly a hundred chromatograms (using the area method) being about 6 %. It is of course always necessary to plot a different graph for each chromatogram.

Accuracy. For solutions containing only cobalt, nickel and copper, the accuracy is equal to the precision, except when only traces of cobalt are present. In the latter case results tend to be slightly high and they must be calculated by the area method. When large amounts of iron are present, the chromatogram must be conditioned in an atmosphere saturated with the developing solvent prior to chromatography, otherwise high results are obtained. The area method of calculation is preferred in this case too, as distortion of the spots may result in erratic results when using the maximum absorbance method.

EXPERIMENTAL

Description of the method

Reagents — Hydrochloric acid, $3N \pm 0.1N$.

Developing solvent: 56 ml acetone + 30 ml *n*-butanol + 12 ml HCl (25 %) + 2 ml acetylacetone (2,4-pentanedione). Prepare from freshly distilled reagents and discard after 3 days.

Spraying solution: 0.03 % solution of rubeanic acid (dithio-oxamide) in ethanol containing 5 % (vol.) conc. ammonia. The ethanol is purified by treating it with $AgNO_3$ and KOH before distillation. Prepare immediately before use.

Apparatus. Glass jars, having a diameter of at least 13 cm and a height of at least 25 cm. The upper edge is ground so that the jar can be closed by a glass plate and the seal made air-tight with desiccator grease.

Micropipette delivering exactly 10 μl.

All-glass spraying gun.

Beckman spectrophotometer DU with special adapter or Photovolt Densitometer Model 525.

Procedure. A standard solution containing 0.1 % Co is prepared by dissolving $CoCl_2 \cdot 6H_2O$ in $3N$ HCl. Solutions containing 20, 16, 12, 8 and 4 mg Co in 100 ml $3N$ HCl are made from this by dilution with $3N$ HCl. A solution of the unknown is prepared containing 4-20 mg Co per 100 ml $3N$ HCl. To dissolve the sample, HNO_3 may be used. The solution is evaporated on the water bath and the residue redissolved in $3N$ HCl. All dilutions must be done with $3N$ HCl.

A sheet of Whatman No. 1 filter paper, measuring 23 × 23 cm is attached in a frame. On the sheet a fine pencil line has been drawn, perpendicular to the machine direction of the paper and at about 5 cm from one of the sides. On this line 8 equidistant points are marked. At each of these points exactly 10 μl of solution are spotted on the paper. 4 of the spots are unknowns (either identical or of different concentrations) and 4 are standards (*e.g.* 20, 16, 12 and 8 mg Co/100 ml).

The sheet is maintained at room temperature and protected from draughts until the spots are completely dry (about 3/4 hour).

It is then fastened together with white cotton thread in the shape of a cylinder, the edges of which must not touch. If the relative air humidity in the room is markedly different from 65 % the cylinder should be conditioned in a constant-humidity cabinet at 65 % R.H. for at least 1 hour and immediately transferred to the chromatography jar. If the cobalt is accompanied by large amounts of iron, conditioning for at least 6 hours in an atmosphere saturated with respect to the developing solvent is always necessary (in which case prior conditioning at 65 % R.H. is of course superfluous). This can easily be achieved by suspending the paper cylinder in the chromatography jar, so that it does not touch the solvent level. Chromatography is carried out by lowering the paper in the solvent. It is allowed to proceed for at least two hours. Optimum resolution is achieved after about 2 1/2 hours but the paper may be left in the jar overnight. The paper cylinder is dried at room temperature under a hood (a fan may be used but heating should be avoided as it always results in slight discoloration of the paper). It is then placed for a few seconds in a jar containing a dish filled with conc. ammonia in order to neutralize any residual acidity. The cotton threads are cut and the paper is again attached in a frame placed under a hood. It is then sprayed lightly and evenly first on one side and, after drying, on the other side with the freshly-prepared spraying reagent. An all-glass spray gun operating under a nitrogen pressure of about 1 atm. is used. The paper should become thoroughly wet, but not dripping. After drying at room temperature, the paper is cut in 8 strips 20 mm wide. Each strip should contain the starting point and the corresponding cobalt spot, exactly centred. As the colour is indefinitely stable it can be measured at any convenient time.

When the Beckman DU spectrophotometer is used, the strips are attached end to end with adhesive tape and the resulting film is fed through the special adapter.

The wavelength dial is set at 422 mμ. Readings are taken at 2 mm intervals over a distance extending for a few cm in front of and behind each cobalt spot. The minimum slit width allowing 100 % transmission with the blank paper in front of the light beam is used. The absorbance (optical density) versus distance is plotted on graph paper. For each peak the best apparent base line is drawn and the area under the peak is measured by means of a planimeter. Using the values found for the standards, a nearly straight line can be drawn, giving the relation between the area and the concentration. The unknown concentrations are calculated from this curve and averaged.

When the Photovolt Densitometer Mod. 525 is used, the strips need not be connected and the absorbance curves are plotted directly on a paper attached to the scanning stage. The paper strips are held in position between two plastic strips, the lower of which has a groove exactly 20 mm wide. A 420 mμ gelatin filter is placed in front of the search unit. With the galvanometer set at maximum sensivity, balancing is easy. Scanning is at 1 mm intervals. The calculations are the same as when the Beckman instrument is used.

Practical applications

(a) Determination of cobalt in the presence of nickel and copper.

Solutions were prepared containing identical amounts of cobalt, nickel and copper in 3*N* HCl. Five chromatograms were run, each with 4 standard spots of pure Co solutions and 4 spots of solutions containing Co, Ni and Cu (range 4-20 mg/100 ml). No systematic differences could be detected between the readings for both sets.

(b) Determination of small amounts of cobalt in nickel.

A 2 % solution was prepared from a synthetic nickel sample containing 0.2 % cobalt. 4 chromatograms were run, each carrying 4 spots of the 2 % unknown solution and 4 standards (6, 6, 4, 4 mg Co/100 ml). The average cobalt content found was 0.210 % (+ 5 %). Standard deviation of the mean of each chromatogram: 0.005 %.

(c) Determination of cobalt in high-speed steels.

Two British Chemical Standards * were analysed: No. 241 containing, according to the certificate, W 20.28, Co 5.84, Cr 5.12, V 1.54, C 0.83, Mo 0.54, Mn 0.23, Si 0.22, Ni 0.19, Cu 0.15, Sn 0.035, S 0.035, P 0.025 %. No. 220 containing: W 7.64, Cr 4.61, Mo 4.17, V 1.35, C 0.86, Co 0.67, Si 0.30, Mn 0.25, Ni 0.15, Cu 0.14.

The following results were obtained:

BCS 241 (16 chromatograms) 6.05 % Co (+ 3.6 %). Standard deviation of the mean of each chromatogram: 0.40.

BCS 220 (16 chromatograms) 0.68 % Co (+ 1.5 %). Standard deviation of the mean of each chromatogram: 0.037.

It may be noted that for chemical analysis the standard deviation between 8 laboratories was resp. 0.087 and 0.017.

ACKNOWLEDGEMENT

We should like to thank Prof. E. MAES, Chief of the Laboratory for permission to publish this paper.

SUMMARY

Cobalt can be determined in the presence of other elements by chromatography followed by photometric scanning. The chromatographic solvent used is a mixture of acetone, *n*-butanol, hydrochloric acid and acetylacetone, and the cobalt spot is

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* Issued by the Bureau of Analysed Samples, Ltd., 234 Marton Road, Middlesbrough, England.

made visible by spraying with a solution of rubeanic acid. The filter paper is cut in strips which are scanned along their length either in a Beckman DU spectrophotometer or a Photovolt densitometer Mod. 525 at 422 mμ. The absorbance curves are plotted and the Co concentration is calculated from the area under the peaks. Chromatograms with 8 spots, each containing 0.4 — 2 μg Co, of which 4 are standards, are convenient. The coefficient of variation for the mean of a single chromatogram is 6 %. Alloys containing as little as 0.2 % Co can be analysed with an accuracy of 5 % or better.

RÉSUMÉ

Il est possible de doser le cobalt en présence d'autres éléments par chromatographie et photométrie directe. Le solvant utilisé est un mélange d'acétone, *n*-butanol, acide chlorhydrique et acétylacétone; le cobalt est rendu visible au moyen d'une solution d'acide rubéanique. Le papier filtre est découpé en bandes le long desquelles on mesure la densité optique au moyen d'un spectrophotomètre Beckman DU ou d'un densitomètre Photovolt Mod. 525 à 422 mμ. On établit les courbes de densité optique et la concentration du cobalt peut être déduite de la surface occupée par les sommets. Des chromatogrammes à 8 taches, chacune contenant 0.4 — 2 μg Co, dont 4 étalons, conviennent très bien. Le coefficient de variation de la moyenne d'un seul chromatogramme est de 6 %. Des alliages contenant au moins 0.2 % de cobalt peuvent êtres analysés à 5 % près ou mieux.

ZUSAMMENFASSUNG

Kobalt in Anwesenheit anderer Elementen kann bestimmt werden durch Chromatographie und photometrische Abtastung der Flecken. Die verwendete Lösung ist eine Mischung von Aceton, *n*-Butanol, Salzsäure und Acetylaceton, die Flecken werden sichtbar gemacht durch eine Lösung von Rubeanwasserstoffsäure. Der Papierbogen wird in Streifen aufgeschnitten, welche in einem Beckman DU Spektrophotometer oder in einem Photovolt Mod. 525 Densitometer bei 422 mμ abgetastet werden. Die Extinktionskurven werden aufgezeichnet und der Kobaltgehalt wird ermittelt durch Ausmessung der Flächen der Gipfel. Chromatogramme mit 8 Flecken, davon 4 Leitflecken bekannten Gehaltes, 0.4—2 μg Co enthaltend, sind bequem. Die relative Streuung des Mittels eines Chromatogramms ist 6 %. Der Kobaltgehalt von Legierungen mit mindestens 0.2 % Co kann bis auf 5 % genau oder besser bestimmt werden.

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DERIVATIVES OF ANTHRARUFIN, CHRYSAZIN AND QUINIZARIN AS COLORIMETRIC REAGENTS FOR BORON

by

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Existing colorimetric methods for the determination of boron leave much to be desired, either because of the laboriousness of the procedures or the lack of sensitivity or precision inherent in the color reaction itself. The oldest colorimetric reagent for boron is curcumin, the coloring principle in turmeric, which was only in recent years made the basis of a precise colorimetric method by NAFTEL[8]. This compound and the tetrahydroxyanthraquinone, quinalizarin, are the reagents which have been most used for the colorimetric determination of traces of boron in soils and plant material. A procedure employing quinalizarin[3] has been adopted as the official method for this purpose by the Association of Official Agricultural Chemists[1]. More recently, methods based on the color reaction of borate with chromotrope-B[2], carmine[7], and 1,1′-dianthrimide[5] have been proposed. The curcumin method requires time-consuming evaporations at controlled temperatures; the chromotrope-B reaction is subject to influence by temperature variation, and is interfered with by a number of cations and anions.

Aside from curcumin and chromotrope-B, virtually all of the important colorimetric reagents for boron are anthraquinone derivatives, and with the exception of 1,1′-dianthrimide, these are hydroxy derivatives of anthraquinone. The anthraquinone reagents require the use of strong sulfuric acid as the solvent in which the color reaction takes place. This is a disadvantage, but is not a serious one if the procedure is not so involved as to make the handling of the strong acid especially inconvenient or hazardous. The dianthrimide reaction is sensitive, and the spectral absorption characteristics of the reagent and its boron complex are favorable for the precise determination of the element, but heating for several hours is needed to develop the color. With the hydroxy-anthraquinones, on the other hand, color development takes place relatively rapidly at room temperature, and they are therefore to be preferred provided the color reaction is such that good sensitivity and precision can be attained.

In addition to quinalizarin, many hydroxyanthraquinones have been observed to give color reactions with borate in concentrated sulfuric acid solution. FEIGL[6] has recorded the color changes thus obtained with a number of di- and tri-hydroxy derivatives of anthraquinone, and several substituted hydroxyanthraquinones have been investigated for the quantitative determination of boron. Among the latter are alizarin sulfonic acid[4] and carmine red[7]. Quinalizarin, however, is the compound of this class which has been the subject of the most extensive investigation, and it has achieved the most extensive use as a colorimetric reagent for boron.

Without exception, the hydroxyanthraquinones and their derivatives dissolve in concentrated sulfuric acid to yield solutions which are themselves highly colored, even in the absence of boric acid. Thus a "two-color" system is obtained upon reaction of borate with the organic compound, since in analytical practice the latter must necessarily be present in excess. With the simple hydroxyanthraquinones, the color reaction takes place without a pronounced change in hue. The spectral absorption curves of the reagent and the boron complex, respectively, overlap markedly, with absorption maxima in the visible region which are not widely separated. This is illustrated by the transmission curves of quinalizarin and its borate complex, which are reproduced in Fig. 1. Visually, the color change with this reagent is from violet to blue; the solution of the unchanged reagent has its absorption maximum at 575 mμ, while that of the colored complex has its maximum at 605 mμ. The overlapping of the absorption bands is so severe that at the latter wavelength the extinction coefficient of the reagent is about sixty-five per cent as large as that of the blue boron complex. For analytical purposes, such an overlapping of the transmission curves of reagent and colored complex is an obvious disadvantage.

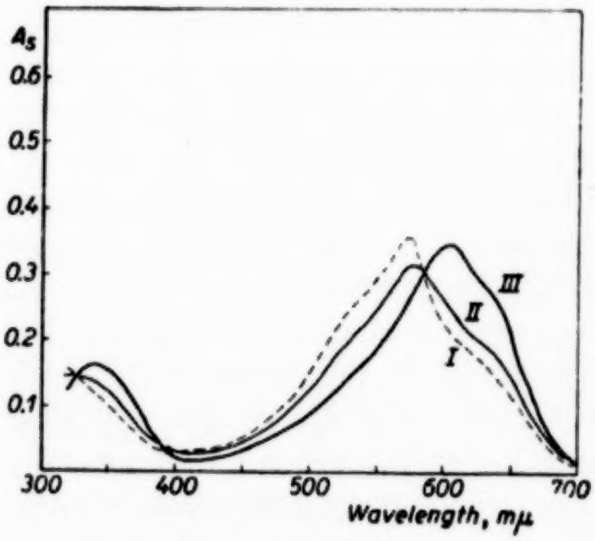

Fig. 1. Quinalizarin.
I. Reagent, 0.005 mg/ml (violet)
II. 0.2 microgram B/ml (blue-violet)
III. 10 micrograms B/ml (blue)

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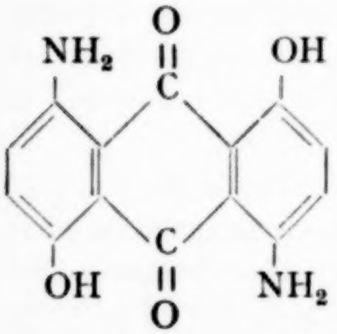
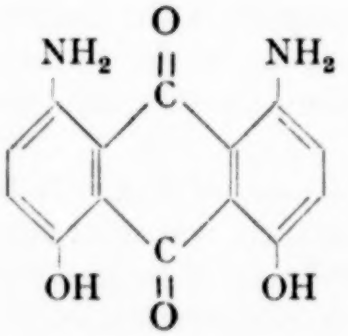
In an effort to discover new reagents with spectral absorption characteristics more favorable for the colorimetric determination of boron, certain hydroxyanthraquinone derivatives with amino, nitro, cyano and halogen substituents were examined. Six compounds of this type, derived from the dihydroxyanthraquinones anthrarufin, chrysazin and quinizarin gave especially striking color reactions.

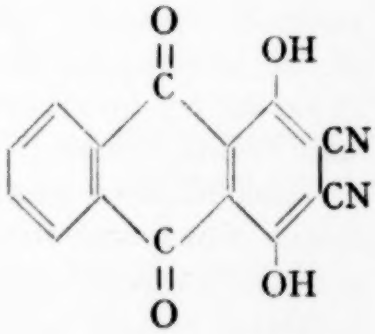
Anthrarufin is the common name for 1,5-dihydroxyanthraquinone. Chrysazin is its isomer with the hydroxyl groups in the 1 and 8 positions, while quinizarin has the two hydroxyls in positions 1 and 4. The derivatives under investigation are: diaminoanthrarufin (1,5-diamino-4,8-dihydroxyanthraquinone), diaminochrysazin (1,8-diamino-4,5-dihydroxyanthraquinone), dinitroanthrarufin (1,5-dinitro-4,8-dihydroxyanthraquinone), dinitrochrysazin (1,8-dinitro-4,5-dihydroxyanthraquinone), tribromoanthrarufin (1,5, (?)-tribromo-4,8-dihydroxyanthraquinone), and dicyanoquinizarin (2,3-dicyano-1,4-dihydroxyanthraquinone). The structural formulas for the diamino derivatives of anthrarufin and chrysazin, and the dicyano derivative of quinizarin are:



Diaminoanthrarufin
I



Diaminochrysazin
II



Dicyanoquinizarin
III

The dinitro derivatives of anthrarufin and chrysazin have structures corresponding to Formulas I and II, respectively, with nitro groups in place of the amino groups. In the tribromoanthrarufin, two of the bromine atoms are in the 1 and 5 positions, but the location of the third bromine atom is at present uncertain.

This paper describes an investigation of the spectrophotometric characteristics of these six compounds and their borate complexes. In our Laboratory, the primary interest in boron analysis lies in the determination of traces in this element in biological material, and it is with this objective that the color reactions of these reagents were studied. The application of the better reagents of this group to the determination of microgram quantities of boron in plant tissue will be the subject of later papers.

APPARATUS AND REAGENTS

Glassware. Glassware employed for the storage and ordinary handling of cold acid solutions was either of the "soft glass" type or made of Corning Alkali Resistant ("Boron Free") Glass No. 7280. The latter type of glassware was employed exclusively for operations requiring heating or evaporation of solutions, and for the storage of alkaline solutions. No evidence of contamination of the solutions or reagents by boron from the glass vessels was ever detected.

Spectrophotometer. Transmission measurements were made with a Beckman Model DU Quartz Spectrophotometer, using matched 1-cm. Corex cells.

Sulfuric acid. The "reagent grade" 95% concentrated sulfuric acid of commerce was used, and all solutions were made up in this medium. Special care is needed in the storage and handling of the solutions to prevent dilution of the acid by absorption of water or discoloration by contamination with dust.

Organic reagents. The hydroxyanthraquinone derivatives were of commercial purity, and were used without further purification. Solutions of the reagents in conc. sulfuric acid containing 0.100 mg or 0.300 mg of reagent per ml were prepared by dissolving weighed amounts of the compounds in appropriate volumes of the solvent. All dissolved readily in the sulfuric acid to a concentration of 0.300 mg per ml except the tribromoanthrarufin, which left a small amount of undissolved residue.

Standard boron solutions. A sample of National Bureau of Standards (U.S.A.) borax which had effloresced slightly was allowed to attain constant weight in a hygrostat over a saturated solution of sodium tetraborate. Analysis of the rehydrated product by acidimetric titration showed it to have a purity of 99.52 %

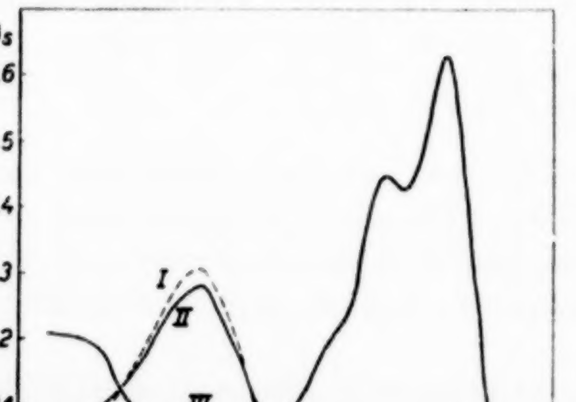


Fig. 2. Diaminoanthrarufin.
I. Reagent, 0.01 mg/ml (yellow)
II. 0.3 microgram B/ml (yellow-green)
III. 5.0 micrograms B/ml (blue)

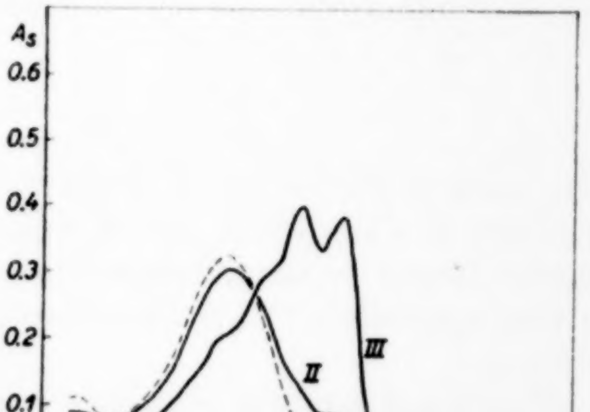


Fig. 3. Diaminochrysazin.
I. Reagent, 0.01 mg/ml (yellow)
II. 0.3 microgram B/ml (orange-yellow)
III. 5.0 micrograms B/ml (orange)

$Na_2B_4O_7 \cdot 10H_2O$. A stock standard solution containing 0.500 mg of B per ml was prepared by dissolving 221.6 mg of the 99.5 % borax in 50.0 ml of conc. sulfuric acid. Working standards were prepared from the stock solution by appropriate dilution.

EXPERIMENTAL

Transmission curves

Transmission curves for the six reagents and their boron complexes are shown in Figs. 2, 3, 4, 5, 6 and 7. In these figures, Curve I is the transmission curve

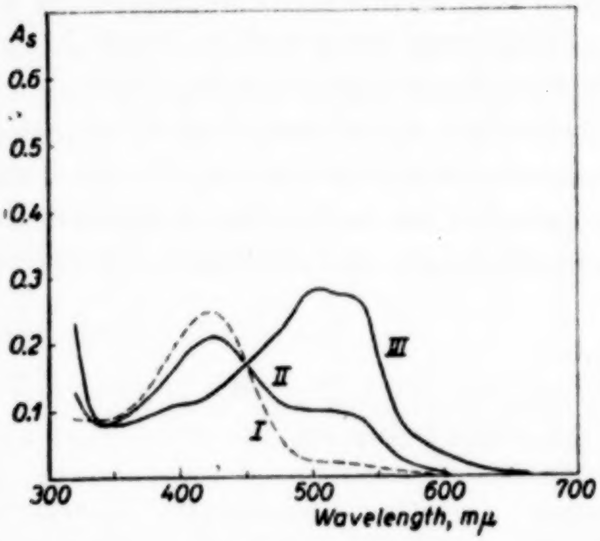


Fig. 4. Dinitroanthrarufin.
I. Reagent, 0.01 mg/ml (yellow)
II. 0.3 microgram B/ml (orange-yellow)
III. 5.0 micrograms B/ml (rose)

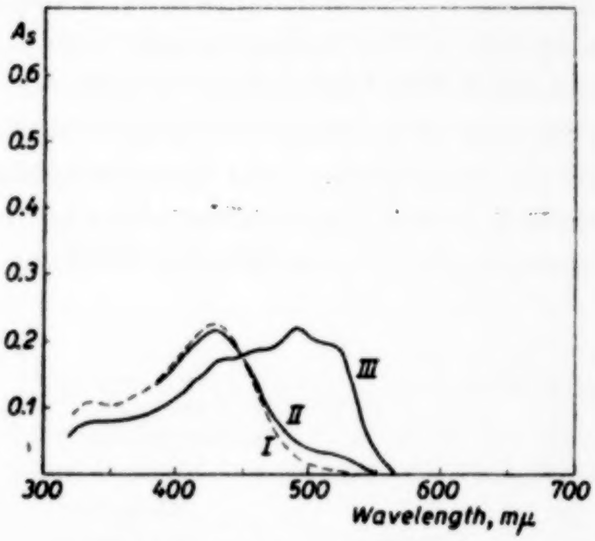


Fig. 5. Dinitrochrysazin.
I. Reagent, 0.01 mg/ml (yellow)
II. 0.3 microgram B/ml (yellow)
III. 5.0 micrograms B/ml (yellow)

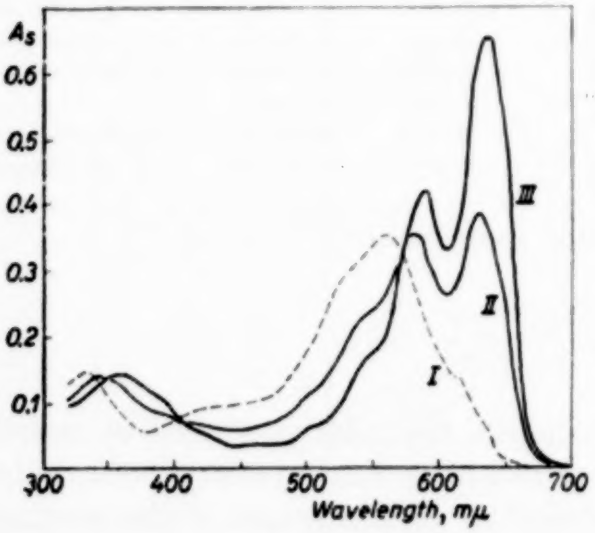


Fig. 6. Tribromoanthrarufin.
I. Reagent, 0.01 mg/ml (violet)
II. 0.3 microgram B/ml (blue-violet)
III. 5.0 micrograms B/ml (blue)

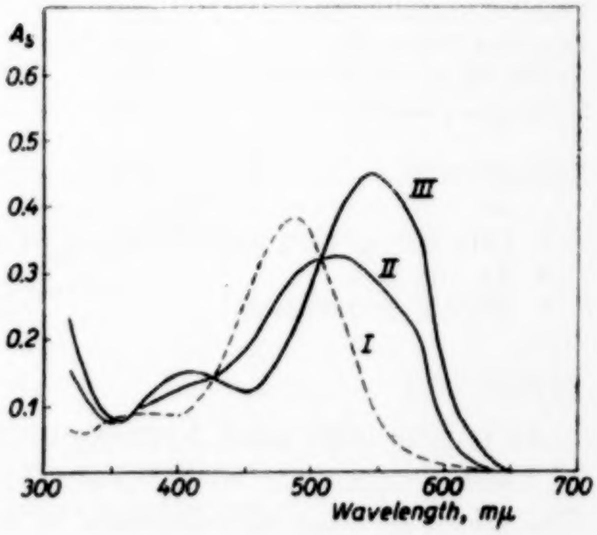


Fig. 7. Dicyanoquinizarin.
I. Reagent, 0.01 mg/ml (orange)
II. 0.3 microgram B/ml (brownish red)
III. 5.0 micrograms B/ml (magenta)

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for a solution containing 100 μg of reagent in a volume of 10 ml. Curve III in each case is that for 10 ml of a solution containing this same quantity of reagent, but with an excess of boron added; and assuming that the conversion of the reagent to its colored complex is essentially complete, this curve represents the absorption curve of the boron complex. The intermediate curve (Curve II) in each figure is the transmission curve of a similar solution containing 0.3 p.p.m. of B (3 μg in 10 ml), in which case, the reagent is present in excess. None of these curves show the very marked overlapping of absorption bands of reagent and colored complex which is characteristic of quinalizarin, though with the cyanoquinizarin, the overlapping is considerable. The wavelengths of maximum absorption of the reagents and their boron complexes are listed in Table I. Also recorded here is the ratio of extinction coefficient of reagent to that of its boron complex at the wavelength at which the latter is a maximum. This is a measure of the overlapping and the consequent reagent blank. Interference in the boron determination due to absorption by the reagent is least in the case of the diaminoanthrarufin. It is small with all five of the anthrarufin and chrysazin derivatives.

TABLE I

SPECTROPHOTOMETRIC DATA ON NEW REAGENTS FOR BORON (ABSORPTION MAXIMA AND SENSITIVITIES)

Compound	Reagent maximum mμ	Complex maximum mμ	Ratio $\frac{\varepsilon \text{ reagent}}{\varepsilon \text{ complex}}$	Sensitivity μg/cm^2	Practical sensitivity[a]
Diaminoanthrarufin	435	620	0.016	0.0025	1: 40,000,000
Diaminochrysazin	440	495	0.16	—	—
		525	0.044	0.0021	1: 50,000,000
Dinitroanthrarufin	425	505	0.08	0.0022	1: 45,000,000
Dinitrochrysazin	430	490	0.13	0.0068	1: 15,000,000
Tribromoanthrarufin	560	637	0.082	0.0010	1:100,000,000
Dicyanoquinizarin	490	545	0.26	0.0011	
			0.11[b]	0.0010[b]	1:100,000,000
Quinalizarin	575	605	0.65	0.0031[c]	1: 35,000,000

[a] Dilution giving absorbance 0.01 greater than blank.
[b] At 565 mμ.
[c] AOAC procedure[1].

Sensitivities

As is true with most hydroxyanthraquinones, the color produced by reaction of these compounds with borate does not reach its full intensity immediately. The speed of color development is influenced by concentration of the reactants, and the reaction takes place more rapidly if carried out first in a small volume of solution, and then diluted to a volume convenient for spectrophotometric measurement. A technique which has proved convenient in analyses with these reagents

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consists of developing the color in a solution volume of 3 ml (1 ml of reagent solution, 0.3 mg/ml, is added to a 2-ml aliquot of solution analyzed). Under these conditions, the color reaches full intensity in an hour or less, depending on the reagent, and the sensitivity obtained is better than when the color reaction is carried out at higher dilution. A development time of one hour at a volume of 3 ml was adopted as standard for comparison of the sensitivities, and the values recorded in Table I refer to these conditions. The sensitivity listed for quinalizarin is that obtained when this reagent is used in the procedure of the Association of Official Agricultural Chemists[1]; it is included here so that the sensitivities of the new reagents may be seen in comparison. The values in column 5 of Table I are the spectrophotometric sensitivities in μg per cm^2 as defined by SANDELL[9], and were calculated from data obtained with solutions containing boron at a concentration of 0.1 p.p.m. in the final solution on which the absorbance measurement was made. With the exception of the dinitrochrysazin, the sensitivities of all of the reagents are equal to or better than that of quinilizarin. The tribromoanthrarufin and the dicyanoquinizarin are especially sensitive.

Adherence to Beer's law

The color reactions of these anthrarufin, chrysazin and quinizarin derivatives with borate ion do not adhere strictly to Beer's law, but all approach it very closely up to a boron concentration of approximately 0.4 p.p.m. in the final

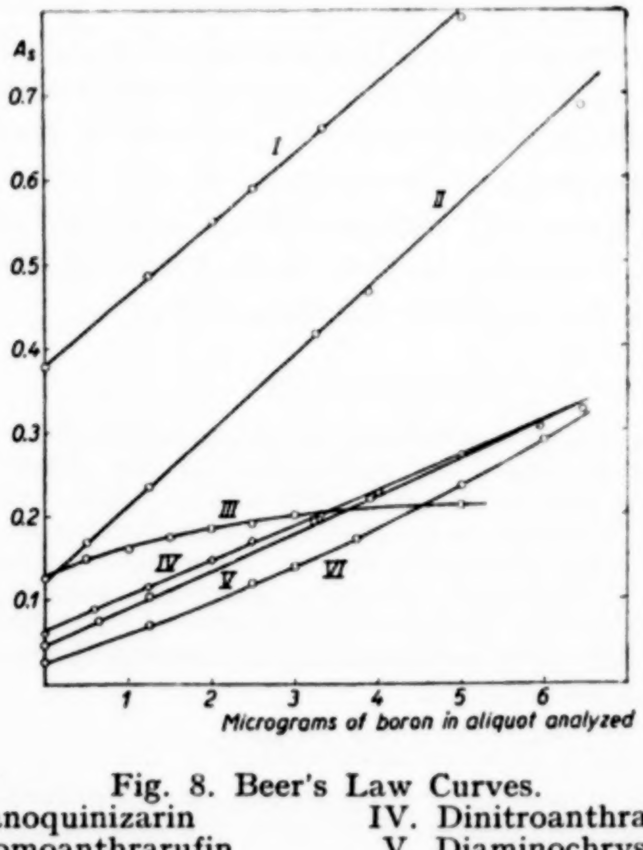

Fig. 8. Beer's Law Curves.

I. Dicyanoquinizarin
II. Tribromoanthrarufin
III. Quinalizarin
IV. Dinitroanthrarufin
V. Diaminochrysazin
VI. Diaminoanthrarufin

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solution (volume 10 ml) on which the color measurement is made. Fig. 8 is a plot of absorbance against concentration of boron for the new reagents. (A curve for the dinitrochrysazin is not included in the figure, because this reagent is the least sensitive of the group and does not appear to have any advantage over the more sensitive ones in the colorimetric determination of boron). Fig. 8 includes for comparison a calibration curve for quinalizarin, obtained by the AOAC procedure. The plot clearly shows that the new reagents give a better proportionality of absorbance to boron concentration (which leads to greater precision in the colorimetric analysis), as well as higher sensitivities.

DISCUSSION

Because of their high sensitivities and favorable spectral absorption characteristics, these anthrarufin, chrysazin and quinizarin derivatives make possible colorimetric methods of high precision for the determination of traces of boron. They are in general similar in chemical behavior and subject to the same interferences as quinalizarin or other hydroxyanthraquinones, and can be substituted with advantage for the latter in procedures for boron determination. The diaminoanthrarufin has been successfully applied to the analysis of some plant materials, and procedures similarly employing the other reagents are being developed. Details of these procedures will be published in subsequent papers.

Derivatives of anthrarufin appear to be especially good in showing a minimum of overlapping of the absorption bands of reagent and boron complex. Halogen and cyano substituents seem to be particularly effective auxochromes in enhancing the sensitivity of the color reaction with borate. Further search for new reagents among these classes of compounds is therefore indicated. Recently, a tetrabromo derivative of chrysazin has been investigated in this Laboratory by YOE AND GROB[10]. This reagent has a very high sensitivity (0.001 μg/cm^2), but the position of its absorption band relative to that of its boron complex is less favorable than is the case with the reagents described here.

SUMMARY

The spectrophotometric characteristics of the color reactions of six new reagents for boron are presented. These are derivatives of the dihydroxyanthraquinones, anthrarufin, chrysazin, and quinizarin, with amino, nitro, cyano, or halogen substituents. The spectral absorption characteristics of these reagents and their borate complexes are much more favorable for the colorimetric determination of boron than is the case with quinalizarin, which is commonly used for this purpose. With the exception of one of the six, all are more sensitive than quinalizarin. Two of them, tribromoanthrarufin and dicyanoquinizarin, are especially sensitive (spectrophotometric sensitivity: 0.0010 μg/cm^2).

RÉSUMÉ

Les auteurs décrivent les caractéristiques spectrophotométriques des réactions colorées de six nouveaux réactifs avec le bore. Il s'agit de dérivés des dihydroxyanthraquinones: anthrarufine, chrysazine et quinizarine renfermant les groupe-

ments amino, nitro, cyano et halogeno. Les caractéristiques de l'absorption spectrale de ces réactifs et de leurs complexes avec le bore sont beaucoup plus avantageuses pour le dosage du bore que celles de la quinalizarine, généralement utilisée. Excepté l'un des six, ces réactifs sont tous plus sensibles que la quinalizarine. Deux d'entre eux, la tribromoanthrarufine et la dicyanoquinizarine, sont spécialement sensibles (sensibilité spectrophotométrique: 0.0010 μg/cm^2).

ZUSAMMENFASSUNG

Die Autoren beschreiben die spektrophotometrischen Eigenschaften der Farbreaktionen von 6 neuen Reaktiven mit dem Bor. Es handelt sich um Derivate der Dihydroxyanthrachinone: Anthrarufin, Chrysazin und Chinizarin, welche Amino-, Nitro-, Cyan- und Halogen-Gruppen einschliessen. Die Eigenschaften der Absorptions-spektren dieser Reaktive und ihrer Komplexe mit dem Bor sind für die Bestimmung von Bor viel vorteilhafter, als die des Chinalizarins, welches normalerweise verwendet wird. Ausser einem dieser Reaktive sind alle viel empfindlicher, als das Chinalizarin. Zwei von ihnen, das Tribromoanthrarufin und das Dicyanochinizarin sind speziell empfindlich (spektrophotometrische Sensibilität: 0.0010 μg/cm^2).

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THE SPECTROPHOTOMETRIC DETERMINATION OF NITRATE IN NATURAL WATERS, WITH PARTICULAR REFERENCE TO SEA-WATER

by

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Nitrate acts as the principal reservoir of combined nitrogen in the sea. Like phosphate, it exerts a controlling influence on marine life. The nitrate in the upper layers of the Arctic and temperate regions may be depleted to the point of exhaustion in summer by the growth of phytoplankton, and its further growth is thus inhibited. The nitrate content of the sea is always relatively low and varies with season, depth, and locality in the range 1-600 mg NO_3-N per m^3.[1]

The determination of nitrate in sea-water is much more difficult than in fresh water, owing to the interference of chloride ion, which prevents the use of most of the commoner colorimetric reagents such as phenol-disulphonic acid[2], or 2,4-xylenol[3].

The earliest determinations of nitrate in sea-water were carried out by reduction to ammonia, which was distilled off and determined by Nesslerisation[4,5], or by oxidation with alkaline hypobromite to nitrogen, the volume of which was measured[6,7]. HARVEY[8] has criticized these methods on the grounds that the results are subject to a systematic error, caused by the drastic conditions of the reduction and subsequent distillation which decomposes amino-acids and albuminoid matter, liberating ammonia.

HARVEY[8,9] has applied a colorimetric test for nitrate and nitrite, first described by DENIGÈS[10], to the determination of nitrate (+ nitrite) in sea-water. This depends on the oxidation of strychnidine (a reduction product of strychnine) in strong sulphuric acid to a red compound. The method has been criticized on the following grounds:

(i) the difficulty of preparing a reliable reagent of satisfactory sensitivity,
(ii) the capricious nature of the reaction,
(iii) its lack of specificity — other oxidizing agents also react,
(iv) interference by dissolved or suspended organic matter.

These criticisms have been answered by ATKINS[11] who has summarized earlier work with this reagent, which has continued to be used *faute de mieux* by many later investigators. Several workers[12-15] have endeavoured to prepare a more reliable reagent. ZWICKER AND ROBINSON[16] have claimed that a more sensitive and reproducible reagent can be prepared using pure crystalline strychnidine. They also found that bistrychnidyl is approximately twice as sensitive but that it is too easily oxidized by oxygen to be satisfactory for routine use.

ATKINS[11] has investigated the use of diphenylbenzidine in strong sulphuric acid as a colorimetric reagent for the determination of nitrate in sea-water. Although WATTENBERG[17] has found that it has a sensitivity similar to strychnidine it does not seem to have come into general use[18], owing perhaps to the sensitivity of the colour intensity to change in the final sulphuric acid concentration.

Other colorimetric procedures for the estimation of nitrate in sea-water have been published using diphenylamine[19], and resorcinol[20], but in common with the above methods are only accurate to ± 10% at best and lack specificity.

A polarographic method for the determination of nitrate in sea-water has been developed by CHOW AND ROBINSON[21]. It is based on the observation by KOLTHOFF *et al.*[22] that nitrate is catalytically reduced in the presence of uranyl ions at the dropping mercury electrode. The method though accurate is not suitable for routine use owing to the necessity for deoxygenation of the samples. SCHREIBER[23] has employed a biological method for the estimation of nitrate in sea-water.

Since nitrite can be simply and accurately determined by the very sensitive colorimetric GRIESS-ILOSVAY method, the reduction of nitrate to nitrite could be used as a specific method for the determination of nitrate. The main problem involved in the development of such a method is that of finding a reagent which, while giving a high yield of nitrite, does not carry the reduction beyond this stage. FØYN[24] reduced nitrate to nitrite in sea-water by warming with granulated zinc on a boiling water bath; the heating period was carefully controlled since reduction beyond the nitrite stage occurred. The maximum yield of nitrite was only *ca.* 10% of the nitrate present. He made no observations on the effect of the reducing agent on pre-existing nitrite, which may amount up to *ca.* 5-10% of the nitrate present. A reducing agent consisting essentially of zinc powder and acetic acid in the presence of manganese sulphate has been suggested by BRAY[25], and subsequently used for the determination of nitrate in plant materials[26] and soils[27]. This method has been found to be insufficiently sensitive to be used for the determination of nitrate in sea-water, since only about a 4% yield of nitrite was obtained.

As a preliminary to the present work, a study has been made of the use of metallic amalgams for the reduction of nitrate to nitrite in distilled water. The amalgam (1 ml) was vigorously shaken in a 250 ml stoppered flask with 100 ml of water containing 1 mg NO_3-N/l. At suitable intervals 5 ml portions of the solution were withdrawn and the nitrite contents measured by the method of MELLON AND RIDER[28]. No nitrite was formed with zinc, cadmium or antimony amalgams. Up to 70% reduction occurred using sodium and lithium amalgams (0.72% Na and 0.05% Li respectively), but the yield of nitrite varied considerably with the amount of amalgam used, and tended to decrease on further shaking with the amalgam. More consistent results were obtained using barium amalgam (0.32% Ba), which gave a yield of 69-72% of nitrite, which was independent of the quantity of amalgam used and of the alkalinity of the solution. The study of barium amalgam was not continued beyond this stage, since its use in sea-water leads to the formation of finely divided barium sulphate which is difficult to remove; it is probable, however, that it would make a serviceable reagent for the determination of nitrate in fresh waters.

A study of the reduction of nitrate by several other reducing agents showed that hydrazine in alkaline solution produced nitrite in good yield (*ca.* 85%). When this reagent was applied to the determination of nitrate in distilled water, it was found that the yield of nitrite varied from day to day. This erratic behaviour was traced to the presence of variable amounts of copper in the distilled water used.

The catalytic effect of copper on the reduction was investigated by carrying out the reaction in the presence of known quantities of copper. To 40 ml portions of a solution containing 250 μg NO_3-N/l and varied amounts of copper (added as copper sulphate), were added 1 ml of 0.3% hydrazine sulphate solution and 1 ml of *N* sodium hydroxide. After standing for either 10 minutes or 4 hours, 2 ml of acetone were added to complex any hydrazine remaining. The nitrite formed was then determined by the method of MELLON AND RIDER, as described in the experimental section. The optical densities of the solutions (final volume 50 ml), measured at 520 mμ in 1 cm cells are shown below.

The results indicate that in the absence of added copper no production of nitrite occurs. The presence of only 0.025 p.p.m. of copper is sufficient to propagate the reaction. At copper concentrations of over 0.5 p.p.m. visible precipitation of cuprous oxide occurred. A further study of the reaction showed that the quantity of copper needed for maximum and reproducible yields was about 6 μg of Cu^{+2} /40 ml and that the amount was not critical.

Copper present (μgCu)	0	0.5	1	2	3	4
Optical density*	0.001	0.013	0.015	0.045	0.122	0.212
Optical density**	0.001	0.085	0.253	0.403	0.444	0.440
Copper present (μgCu)	5	6	7	8	9	10
Optical density*	0.323	0.350	0.375	0.385	0.385	0.383
Optical density**	0.446	0.458	0.452	0.454	0.458	0.461
Copper present (μgCu)	12.5	15	17.5	20		
Optical density*	0.376	0.375	0.365	0.373		
Optical density**	0.469	0.460	0.450	0.454		

* 10 minutes reduction. ** 4 hours reduction.

Experiments were then made using this concentration of copper (6 μg Cu^{+2}/40 ml) and the conditions described above, to determine the optimum amounts of hydrazine sulphate and sodium hydroxide. It was found that an 85% yield of nitrite was obtained in 2 hours using 0.8 ml of 3% hydrazine sulphate and 1 ml of N sodium hydroxide per 40 ml sample.

When the effect of foreign ions on the method was examined it was found that the reduction proceeded rapidly in the presence of 3% of sodium chloride or potassium sulphate and of 0.04% of calcium chloride. It was completely inhibited by magnesium at a concentration (0.0001% Mg) not great enough to give a visible precipitate of magnesium hydroxide at the pH of 12.1 at which the reduction was carried out. Since sea-water contains *ca.* 0.13% of magnesium it was necessary to modify the method before it could be applied to the determination of nitrate in sea-water.

Attempts were made to remove magnesium by precipitation as magnesium ammonium phosphate, hydroxide, or fluoride. But, although the filtrates permitted a 40-50% conversion of nitrate to nitrite, the procedure was not suitable for routine use, and gave erratic results. The possibility of using chelating agents to prevent the precipitation of magnesium hydroxide was next investigated. Citrate, tartrate, and ethylenediamine tetraacetate, while retarding or preventing the precipitation, also completely inhibited the reduction of nitrate to nitrite, owing perhaps to their having also chelated the copper catalyst. Hexametaphosphate prevented the precipitation of the salts, but nitrite was not formed until hydrolysis of the hexametaphosphate had reduced the pH of the solution to below 10, and even then the yield was low.

The precipitation of magnesium from sea-water begins to be apparent at *ca.* pH 10, but its inhibiting effect on the reduction of nitrate by hydrazine becomes evident above pH 9.6. Attempts were made to carry out the reduction at pH 9-9.5, and it became immediately obvious that it was essential to buffer the solution, since the hydrogen ion liberated from the hydrazine sulphate during the reaction often decreased the pH to below 7. At these lower pH values nitrite is rapidly destroyed by hydrazine. The choice of a suitable buffer was difficult: ideally a buffer for pH 9-9.5 can be prepared from either a weak base (K_B = *ca.* 10^{-5}) and its salt with a strong acid, or a weak acid (K_A = *ca.* 10^{-10}) and its sodium salt. For the reaction under consideration, the choice of suitable bases or acids is rather limited. Of the former class, ammonia, substituted ammonias and piperidine proved unsuccessful. Of the weak acids of suitable dissociation constant, arsenious, boric and carbonic acids were unsatisfactory owing to the insolubility of their calcium and magnesium salts. Phenol ($K_A = 0.97 \cdot 10^{-10}/25°$)[29] however, yielded a buffer having the desired pH, which did not give precipitates with either calcium or magnesium at the concentrations at which they occur in sea-water.

Effect of alkalinity on the reduction of nitrate by hydrazine in sea-water

Portions of sea-water (40 ml) were placed in 50 ml graduated flasks and treated with 2 ml volumes of sodium-phenate buffer (containing 1 ml of 0.4*N* phenol and varied volumes of 0.5 *N* sodium hydroxide per 2 ml). After the addition of 0.5 ml of copper sulphate solution (20 µg Cu/ml) and 0.5 ml of 0.48% hydrazine sulphate solution, the solutions were mixed and set aside in the dark for 24 hours.The determination of nitrite was performed as described in the experimental section, except that the acidity of the sulphanilic acid was adjusted so that the pH used for the coupling of the diazonium salt was 2.0-2.3. A duplicate series of determinations was carried out on samples of the same sea-water enriched with 250 µg NO_3-N/l. The results (Table I) showed that maximum colour formation was only attained in 24 hours when a buffer containing from *ca.* 0.62 to 0.7 ml of 0.5*N* sodium hydroxide and 1 ml of 0.4 *N* phenol was used. At lower alkali concentrations, the reduction was much slower and was not complete in this time. More than 0.7 ml of 0.5*N* sodium hydroxide in the buffer solution caused precipitation of calcium and magnesium salts, which completely inhibited the reduction. In all subsequent work 2 ml of a buffer containing the equivalent of 1 ml of 0.4*N* phenol and 0.64 ml of 0.5*N* sodium hydroxide was used.

TABLE I

EFFECT OF VARIATION OF SODIUM HYDROXIDE TO PHENOL RATIO ON REDUCTION OF NITRATE BY HYDRAZINE

ml 0.5 *N* NaOH	0.4	0.5	0.6	0.62	0.64	0.66	0.7	0.8	1.0 **
Sea-water*	0.070	0.077	0.077	0.075	0.076	0.076	0.084	0.068	0.011
Sea-water + 250 µg NO_3-N/l*	0.350	0.394	0.422	0.429	0.431	0.429	0.447	0.057	0.015
Difference*	0.280	0.317	0.345	0.354	0.355	0.353	0.363	0.009	0.004
pH for reduction	9.10	9.35	9.52	9.58	9.61	9.64	9.69	9.82	9.98
pH of solution without $N_2H_4.H_2SO_4$	9.29	9.52	9.68	9.72	9.76	9.80	9.85	9.96	9.96

* Optical densities measured in 1 cm cells at 524 mµ.
** Visible precipitation of magnesium and calcium salts.

Effect of variation of hydrazine sulphate concentration

In order to investigate the effect of the variation of the hydrazine sulphate concentration, 40 ml portions of sea-water (enriched with 250 µg NO_3-N/l) were treated with 2 ml of phenol-sodium phenate buffer, 10 µg of copper, and varied volumes of 0.3% hydrazine sulphate solution. The nitrite formed after various reduction periods was determined, after the addition of acetone to complex any unreacted hydrazine, by the method of MELLON AND RIDER. It was found that the reaction rate and yield of nitrite were independent of the hydrazine concentration in the range corresponding to the addition of 0.75-1.0 ml of 0.3% hydrazine sulphate solution. With less than 0.75 ml of 0.3% hydrazine sulphate the dissolved oxygen in the solution destroyed all the hydrazine within 3 hours and thus greatly diminished the yield of nitrite. Too great an excess of hydrazine sulphate also resulted in lower yields of nitrite. In all subsequent work an amount of hydrazine sulphate, equivalent to 0.8 ml of 0.3% hydrazine sulphate, was used.

Effect of variation of copper concentration

The copper content of sea-water (1.5-25 μg Cu/l[30,31]) is considerably below the concentration needed to catalyse the reduction of nitrate to nitrite in distilled water. The effect of copper on the reduction in sea-water was therefore investigated. Samples (40 ml) of sea-water (original copper content 22 μg Cu/l) to which varied amounts of copper had been added (as copper sulphate) were treated with 2 ml of phenol-sodium phenate buffer and 1 ml of 0.24% hydrazine sulphate solution. After 24 hours, 2 ml of acetone were added and the nitrite formed was determined as described on p. 475. Similar experiments were carried out using the same sea-water enriched with 210 μg NO_3-N/l. The results, which are shown graphically in Fig. 1, indicated that the marked effect of copper on the reduction in distilled water was also shown in sea-water. Even without the addition of copper some reduction of nitrate occurred, owing to the presence of copper in the original sea-water. When the curves were produced back to zero optical density, they cut the abscissa at 0.9 μg of copper, *i.e.*, at a concentration of 22.5 μg Cu/l, a value which agreed well with that found in the water by a chemical method (22 μg Cu/l)[32]. Hence it appears that copper is the only substance present in sea-water in amounts sufficient to catalyse the reduction. Maximum reduction in sea-water, amounting to *ca.* 69% conversion of nitrate to nitrite, occurred with 5 μg Cu/40 ml. Above this concentration the yield of nitrite gradually declined. In all subsequent work 1 ml of

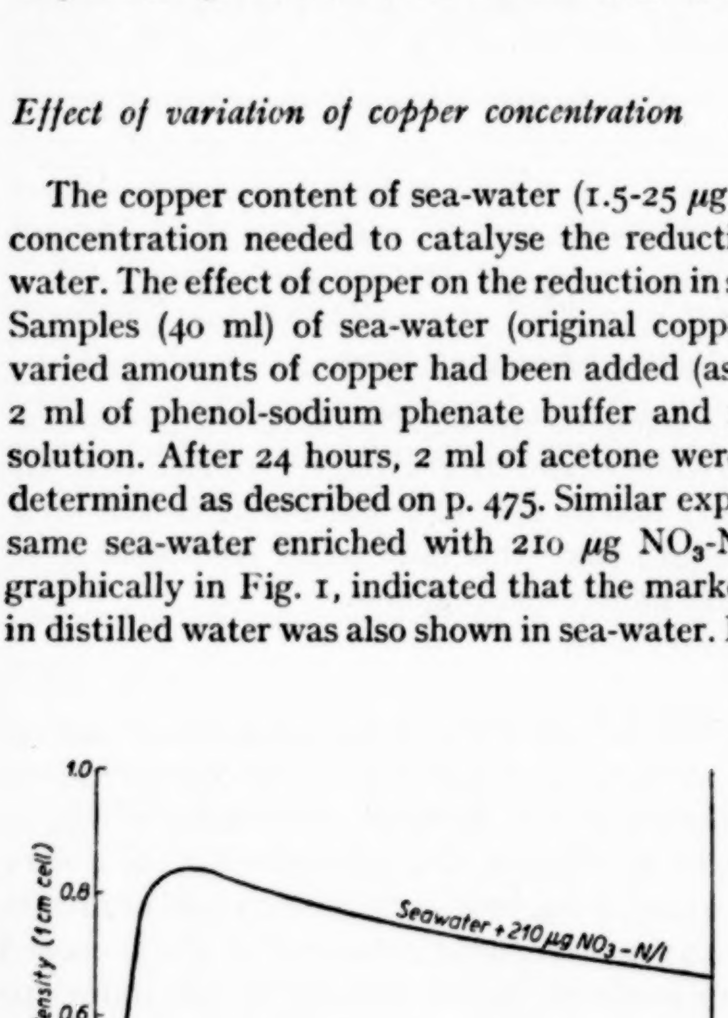

Fig. 1 Effect of copper concentration on reduction of nitrate by hydrazine in sea-water.

copper sulphate solution containing 10 μg Cu/ml was added to each determination.

The reduction is complete in both fresh and sea waters in approximately 22 hours at 20°, and no increase or decrease in the nitrite formed occurs for at least a further 20 hours.

Effect of temperature on the reduction

Distilled water and sea-water samples containing 250 μg NO_3-N/l were reduced at various temperatures by the proposed method, giving the results shown below:

Optical densities*	15°	20°	25°	30°
Distilled water + 250 μg NO_3-N/l	0.464	0.469	0.486	0.487
Sea-water + 250 μg NO_3-N/l	0.317	0.358	0.350	0.349

* at 524 mμ, 1 cm cell, after deduction of reagent blank.

It will thus be seen that increase in temperature slightly enhances the optical density in distilled water, but in sea-water causes little change, provided that the temperature is not below 18°. The reduction should not be carried out in sea-water at temperatures much in excess of 30°, since this may cause precipitation of calcium and magnesium salts, which inhibit the reaction.

Salt error effect

The salts present in sea-water reduce the efficiency of the reduction of nitrate to nitrite (Fig. 2 p.475); this salt error has been investigated at nitrate concentrations of 375 and 37.5 μg NO_3-N/l using waters of four different chlorinities, ($Cl^0/_{00}$ = 4.75, 9.45, 14.13, and 18.82), prepared by dilution of a sea-water having a very low nitrate content. Samples of the waters (40 ml) were enriched with 1 ml of nitrate solution, and the optical densities were measured, after reduction by the proposed method. Blank determinations were made on 40 ml samples of the waters to which 1 ml of distilled water had been added. It was found that the salt error factor (the ratio of the optical density from the nitrite formed in sea-water to that from the nitrite formed from the same amount of nitrate in distilled water) was a linear function of the chlorinity and independent of the nitrate concentration to within 3%. The average correction factors obtained by interpolation are given below (Table II).

TABLE II

SALT ERROR FACTOR

$Cl^0/_{00}$	0.0	5.0	10.0	15.0	16.0	17.0	18.0	19.0	20.0
Salt error factor	1.00	0.94	0.88	0.82	0.81	0.80	0.78	0.77	0.76

Interference of nitrite

Although the nitrite content of sea-water almost always amounts to less than 5% of the nitrate concentration of the water, it was thought desirable to investigate its fate under the conditions used for the reduction of nitrate. Portions of distilled water and nitrate and nitrite-free sea-water (Cl = $18.79\,^0/_{00}$) were enriched with 1 ml volumes of nitrite solutions of various strengths. The optical densities of the solutions were measured after reduction and colour development by the proposed method.

Replicate determinations showed rather greater variability than was found when nitrate was reduced. The average results are shown in Table III, together with the optical densities obtained at the same nitrite concentrations by the method of MELLON AND RIDER without reduction.

During the reduction with hydrazine, considerable destruction of nitrite occurs, the percentage destroyed is dependent on the amount of nitrite originally present, particularly in sea-water at low nitrite concentrations. Table IV shows the ratio of the optical densities obtained with the proposed method, using nitrite-enriched waters to the optical densities given by the method of MELLON AND RIDER with the same enriched waters.

TABLE III

OPTICAL DENSITIES OF NITRITE SOLUTION BEFORE AND AFTER REDUCTION WITH HYDRAZINE

	Optical densities at 524 mμ in 7.62 cm cell*		
Added nitrite μg NO_2-N/40 ml	MELLON & RIDER	Reduced with hydrazine Distilled Water	 Sea-Water
0.10	0.046	0.032	0.004
0.25	0.114	0.089	0.043
0.50	0.228	0.197	0.089
0.75	0.343	0.300	0.166
1.00	0.456	0.410	0.215
1.50	0.683	0.627	0.298
2.00	0.912	0.843	0.435
2.50	1.400	—	0.548

* Reagent blank deducted.

TABLE IV

RATIOS OF OPTICAL DENSITIES (7.62 cm CELL) OF NITRITE SOLUTIONS WITH AND WITHOUT REDUCTION BY HYDRAZINE

μg NO_2-N/l	1	2	3	4	5	7.5	10	12.5	15
Distilled water	0.63	0.68	0.73	0.76	0.78	0.81	0.84	0.87	0.88
Sea water (Cl = $18.79\,^0/_{00}$)	0.04	0.08	0.14	0.22	0.30	0.37	0.40	0.41	0.42

μg NO_2-N/l	17.5	20	25	30	35	40
Distilled water	0.88	0.89	0.90	0.91	0.92	0.92
Sea water (Cl = 18.79‰)	0.44	0.44	0.45	0.46	0.46	0.47

Analysis of mixtures of nitrate and nitrite

In order to determine whether nitrite had any effect on the reduction of nitrate, sea-waters enriched with equal amounts of nitrate and nitrite nitrogen were analysed for nitrate. The results, which are shown below, indicate that nitrate and nitrite act additively; the results, however, are not as consistent as they are when the ratio of nitrate-nitrogen to nitrite-nitrogen is greater.

NO_2-Nμg/l taken	2.5	6.25	12.5	25.0	37.5
NO_3-Nμg/l taken	2.5	6.25	12.5	25.0	37.5
NO_3-Nμg/l found	2.9	6.2	12.9	27.5	39.8

Method

All measurements of optical density were made with a Unicam S.P. 500 spectrophotometer, using a slit width of *ca.* 0.025 mm. pH measurements were carried out by means of a Cambridge Instruments' pH meter, using a glass electrode.

Reagents:

All reagents and solutions must be made up with water freshly distilled from an all-glass still.

1. *Phenol-sodium phenate buffer.* Dissolve 9.40 g of phenol B.P. in 200 ml of water. Filter through a sintered glass filter (porosity 4) and dilute to 250 ml. Pipette 50 ml of this stock phenol solution into a 100 ml graduated flask, add 16 ml of 1.00*N* sodium hydroxide solution, dilute to volume and mix thoroughly. Store the reagent in a dark glass bottle and reject it when it becomes discoloured.
2. *Copper sulphate catalyst.* Prepare a solution containing 0.0393 g of copper sulphate pentahydrate A.R. per 100 ml.
3. *Hydrazine sulphate solution.* Dissolve 1.20 g of hydrazine sulphate A.R. in *ca.* 240 ml of water. Dilute to 250 ml and filter through a sintered glass filter (porosity 4).
4. *Hydrazine-copper reducing agent.* Mix 25 ml of the stock hydrazine sulphate solution with 5 ml of the copper sulphate catalyst and dilute to 50 ml. This reagent should be prepared daily.
5. *Sulphanilic acid.* To a solution of 0.30 g of sulphanilic acid A.R. in *ca.* 80 ml of water add 12.9 ml of concentrated hydrochloric acid and dilute to 100 ml.
6. *1-Naphthylamine.* Dissolve 0.60 g of recrystallized 1-naphthylamine hydrochloride in *ca.* 80 ml of water containing 1 ml of concentrated hydrochloric acid. Dilute to 100 ml.

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7. *Sodium acetate 2M.* 27.2 g of hydrated sodium acetate/100 ml.
8. *Acetone.* A.R. or B.G.S.
9. *Standard Nitrate solution* (10 μg NO_3-N/ml). 0.0722 g of potassium nitrate A.R./l. Dilute as required.

Treatment of flasks

Clean all graduated flasks which are to be used for the determination of nitrate by filling them with concentrated sulphuric acid. After a few hours, empty them, and rinse first with water, then with dilute (0.1 *N*) sodium hydroxide, and finally wash well with distilled water.

Method

Place 40 ml of the sea-water sample (freshly filtered, through a fine textured filter paper) in a 50 ml graduated flask, and add 2 ml of phenol-sodium phenate buffer while gently swirling the solution. Add 1 ml of the hydrazine-copper reagent, mix thoroughly and set aside in the dark.

After 24 hours, add 2 ml of acetone in order to complex any residual hydrazine and to retard the precipitation of the red azo-dye from nitrate rich sea-waters (containing 300-600 mg NO_3-N/m^3). Allow the reaction to proceed for at least 2 minutes and then add 2 ml of sulphanilic acid reagent with shaking. After not less than 5 minutes add 1 ml of the 1-naphthylamine reagent, shake, and then add 1 ml of 2 *M* sodium acetate. Dilute to 50 ml and mix thoroughly. After 15 minutes measure the optical density of the solution at 524 mμ* (or with a suitable filter) in a cell of appropriate length.

Reagent blank for sea-waters

Since it is frequently impossible to obtain sea-water absolutely free from nitrate, it is necessary to determine the reagent blank in the following fashion. Using 40 ml of water freshly distilled from alkali, determine the optical density of the reagent blank *A* as described above. Determine the optical density *B* of a similarly treated sample of the same distilled water, to which the 1-naphthylamine reagent has not been added. The value for *B* is independent of whether sea-water or distilled water is used. The reagent blank for sea-water $= B + (A - B) \times$ salt error (Table II). This reagent blank should be determined daily. If the nitrate concentration of the water sample is high (above 80 mg NO_3-N/m^3) then it suffices to employ the uncorrected distilled water blank as a reagent blank.

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* The wavelength of maximum absorption of the azo dye in distilled water in the absence of acetone is 520 mμ, acetone (2 ml/50 ml) increases it to 522 mμ. It is raised to 524 mμ in sea-water in the presence of acetone. The variation in optical density over this range of wavelength only amounts to 0.5%.

Calibration

Calibrate the method by adding 1 ml portions of suitably diluted standard nitrate solution to 40 ml samples of sea-water (low in nitrate), and develop the colour as described above. If suitable sea-water is not available use 40 ml of water freshly distilled from alkali instead, and correct the results using the salt error factors given in Table II.

Determination of nitrate in fresh waters

The method described above may be used for the determination of nitrate in fresh waters. Since the nitrate concentrations of such waters are fairly high (up to 10 mg NO_3-N/l), it is necessary to take smaller samples (*e.g.* 5 ml or less) and to dilute to 40 ml with water distilled from alkali before carrying out the reduction. The reagent blank and calibration curve are determined using water distilled from alkali.

CALCULATIONS

In general it is not necessary to correct for nitrite interference in sea-waters if it amounts to less than *ca.* 5% of the nitrate present. In order to make the method of calculation clear a worked out example is given. The following optical densities were recorded using a 7.62 cm cell at 524 mμ.

Calculation with low concentrations of nitrite

Reduction procedure on 40 ml of sea-water sample X (Cl = 18.7$^0/_{00}$) 0.455 (1)
Similar determination on distilled water omitting 1-naphthylamine 0.028 (2)
Reduction procedure on alkali distilled water (40 ml) 0.087 (3)
Nitrate in reagents = (3) — (2) = 0.087 — 0.028 = 0.059
Correcting for salt error (Table II) to chlorinity 18.7$^0/_{00}$
Sea-water blank due to nitrate in reagents = 0.059 × 0.77 = 0.045
Total sea-water blank = 0.045 + 0.028 = 0.073 (4)
This total blank is constant throughout a series of determinations.
Optical density due to nitrate = 0.455 — 0.073 = 0.382
Hence from the calibration curve (Fig. 2) (7.62 cm cell) sample X contains 36.7 μg NO_3-N/l. If the chlorinity of the water sample is appreciably different from 19$^0/_{00}$, the observed optical density of the reduced sample should be divided by the salt error factor (Table II) at the appropriate chlorinity, and the nitrate concentration read from the distilled water calibration curve.

Calculation in presence of high nitrite concentrations

Considering a sea-water rich in nitrite giving the same readings as in (1) and (2) above.

Sample X with MELLON AND RIDER reagents = 0.162* (5)
Calibration with 40 ml of distilled water containing 25 μg NO_2-N/l = 0.456* (6)
hence X contains 8.9 μg NO_2-N/l
NO_2-N correction for this nitrite concentration is 0.39. Hence the nitrite contribution to the absorption of the reduced solution = $0.39 \times 0.162 = 0.063$. Optical density due to total reagent blank (4) and nitrite in sea-water after reduction = $0.073 + 0.063 = 0.136$, hence absorption due to nitrate = $0.455 - 0.136 = 0.319$. Hence, from the calibration curve, the water sample X contains 30.6 μg NO_3-N/l.

* less reagent blank

RESULTS

Calibration curves were prepared using distilled water and sea-water (Cl = $18.82^0/_{00}$, very low in nitrate) enriched by the addition of known amounts of nitrate. The results are shown in Fig. 2; each point is the mean of three determinations, and has been corrected for the blank. There is a linear relationship between

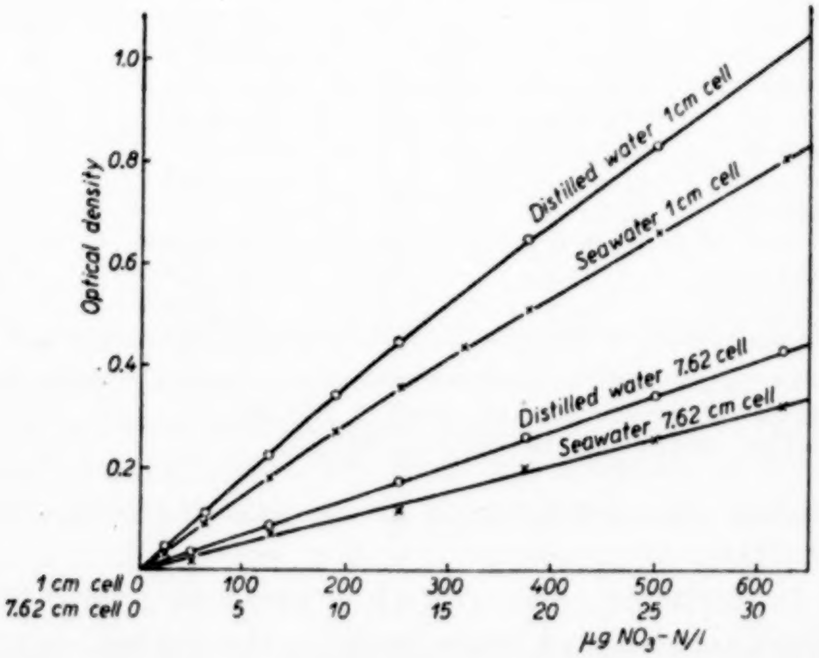

Fig. 2. Calibration curves for determination of nitrate in distilled water and sea-water (Cl = 18.82%).

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optical density and nitrate concentration up to 50 μg NO_3-N/l. Above this concentration, the optical density increment per μg NO_3-N decreases somewhat. Above concentrations of 250 μg NO_3-N/l Beer's law is again obeyed. It is not advisable to work with solutions showing optical densities much greater than 0.7 in a 1 cm cell owing to the instability of the azo-dye suspension, which soon precipitates at these high concentrations even in the presence of acetone. The calibration curves are not affected by the use of fresh batches of reagents, but should be checked periodically at one or two points.

Reproducibility

Replicate determinations (seven) were carried out on a sea-water, before and after enrichment with 25 μg or 250 μg NO_3-N/l, on potable water, and on two typical river waters. For the fresh waters it was necessary to reduce the volume of sample taken owing to their relatively high nitrate content and to the sensitivity of the method. The results are shown in Table V. They show that the reproducibility is good, with a standard deviation of less than 2%. It is most important to filter all samples through a close-textured filter paper before analysis, since it has been found that the presence of even small amounts of suspended matter prevent the full reduction of nitrate to nitrite.

TABLE V

ANALYSIS OF WATER SAMPLES

		Nitrate determination			
Sample	μgNO_2-N/l	Volume ml	Mean optical density	Standard deviation %	Found μgNO_3-N/l
Sea-water	0.5	40	0.003*	30	0.2
Sea-water + 25 μg NO_3-N/l	0.5	40	0.278*	1.8	26.0
Sea-water + 250 μg NO_3-N/l	0.5	40	0.360**	0.3	249
Tap water (Liverpool)	19.4	10	0.754**	1.2	930
River Severn (Upton)	243	2.5	0.441**	1.9	6,600
,, Onny (Onibury)	21.7	7	0.456**	1.8	1,390

* 7.62 cm cell after deduction of reagent blank.
** 1 cm cell after deduction of reagent blank.

Sea-water surface samples collected at five stations in the English Channel off Plymouth[33] (Dates of collection: L 6, E 1, 19/7/54; L 2, L 4, L 5, 11/8/54) were analysed in duplicate alone, and after enrichment with 250 μg NO_3-N/l. The results, which are recorded below, indicate the almost complete exhaustion of the nitrate in the water, normally found in July and August, and the excellent recovery of added nitrate.

Station[33]	E 1	L 2	L 4	L 5	L 6
Found NO_3-Nμg/l	14	3.0	0.0	3.0	0.0
Found NO_3-Nμg/l*	268	260	241	254	247
Difference	254	257	241	251	247

* 250 μg NO_3-N/l added.

Interference of amino acids and certain other nitrogen compounds

Since amino acids and urea react with nitrite in acid solution, their possible interference in the determination of nitrate has been investigated. Sea-water samples containing various amounts of added nitrogen compounds were analysed. Similar analyses were carried out on samples of the same sea-water enriched in addition with known amounts of nitrate. The results are shown in Table VI.

TABLE VI

INTERFERENCE OF NITROGEN COMPOUNDS

			Optical density at 524 mμ (7.62 cm cells)		
Compound	Conc. (p.p.m.)	μgNO_3-N/l added	No added NO_3^-	Added NO_3^-	Difference
Sea-water only	—	25	0.076	0.332	0.256
Sea-water only	—	250	0.010*	0.370*	0.360*
Ammonium chloride	2	25	0.069	0.257	0.188
Ammonium chloride	2	250	0.014*	0.371*	0.357*
Urea	0.2	25	0.085	0.331	0.246
Urea	2	250	0.017*	0.369*	0.352*
Arginine	2	25	0.075	0.335	0.260
Asparagine	2	25	0.081	0.323	0.242
Glutamic acid	2	25	0.073	0.308	0.235
Glycine	2	25	0.076	0.325	0.249
Methionine	2	25	0.075	0.326	0.251

* 1 cm cell.

Ammonium ion and urea interfere with the determination of low concentrations of nitrate, but their interference only becomes appreciable at concentrations of at least 20 times the nitrate-nitrogen, a condition which is never found in sea-water. The amino acids examined (which are representative of the principal types) show little effect at concentrations up to 2 p.p.m.

Storage of samples

It is not always convenient to analyse samples for nitrate immediately after collection. Experiments were therefore carried out to find suitable methods for stabilisation of the nitrate concentration. The addition of either chloroform or formaldehyde completely inhibits the reduction of nitrate to nitrite and prevents their use as preservatives. Mercuric ion has been used for the sterilization of sea-water samples for the determination of nitrate by the strychnidine method[34]. In order to test its efficacy, samples of filtered sea-water were stored in diffused daylight in glass and polyethylene bottles, with and without the addition of 1 p.p.m. of mercuric chloride. Duplicate analyses for nitrate were carried out fortnightly. Similar runs were performed with samples stored in the dark. The results of a typical series of experiments are recorded in Table VII.

TABLE VII

STORAGE OF SAMPLES FOR DETERMINATION OF NITRATE
(Concentrations expressed as μg NO_3-N/l)

	Diffused Daylight				Dark			
	Glass		Polyethylene		Glass		Polyethylene	
Weeks stored	No Hg	+ Hg	No Hg	+ Hg	No Hg	+ Hg	No Hg	+ Hg
0	178	175	178	176	176	178	178	179
2	163	163	156	166	140	162	163	166
4	170	168	135	157	139	168	105	163

There is a general decrease in nitrate content of the waters on storage, particularly those stored in polyethylene bottles in the absence of mercury. The greatest stability was found with samples kept in glass; the presence of mercury had little effect on the nitrate variation of sea-waters stored in glass containers, except in the dark. It should be noted, however, that the samples examined had been filtered (Whatman No. 2 paper) before storage, and it is probable that much greater changes in nitrate concentration would occur with unfiltered samples owing to the decay of suspended organic matter[35]. It is recommended therefore that sea-water samples should be analysed for nitrate within 24 hours of collection; but if this is not possible they should be filtered and stored in glass bottles in the presence of not more than 2 p.p.m. of mercuric chloride.

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SUMMARY

Nitrate can be reduced to nitrite in good yield by means of hydrazine in alkaline solution; the reaction is promoted by catalytic quantities of copper. The authors have established the optimum conditions for the reduction and applied the method to the determination of nitrate in fresh waters and in sea-waters. The nitrite formed is determined by Mellon and Rider's modification of the Griess-Ilosvay procedure. The reduction with hydrazine is carried out in the presence of 0.25 p.p.m. of copper at pH 9.6 in a solution buffered with sodium phenate. It is complete within 24 hours at room temperature. The method will detect *ca.* 0.3 μg NO_3 N/l and gives a standard deviation of *ca.* 2% in the range 20-600 μg NO_3-N/l. Up to 60 determinations can be made per 6 hour working period. The interference of nitrite has been investigated. Ammonium salts, urea, and amino acids do not interfere, at the concentrations at which they occur in sea-water.

It is preferable to analyse samples immediately after collection, but if this is not possible, they should be filtered, sterilized with 2 p.p.m. of mercuric chloride and stored in glass containers.

RÉSUMÉ

Les nitrates peuvent être réduits en nitrites par l'hydrazine en solution alcaline; la réaction est catalysée par le cuivre. Les auteurs ont établi les conditions optimums de cette réduction; ils ont appliqué cette méthode au dosage du nitrate dans les eaux douces et dans les eaux de mer. Le nitrite formé est déterminé par la méthode de GRIESS-ILOSVAY modifiée par MELLON ET RIDER. La réduction à l'hydrazine est effectuée en présence de 0.25 p.p.m. de cuivre, au pH 9.6 en solution tamponnée au phénate de sodium; elle est quantitative après 24 heures, à la température ordinaire. Cette méthode permet de déceler environ 0.3 μg NO_3-N/l; l'erreur est d'environ 2% pour teneurs de 20-600 μg NO_3-N/l. On peut effectuer 60 dosages en 6 heures. L'influence des nitrites a été examinée. Les sels d'ammonium, l'urée et les acides aminés ne gênent pas à leur concentration dans l'eau de mer. Il est préférable d'effectuer les analyses immédiatement après les prélèvements, mais si cela n'est pas possible, les eaux devraient être filtrées, stérilisées avec 2 p.p.m. de chlorure mercurique et conservées dans un récipient en verre.

ZUSAMMENFASSUNG

Die Nitrate können mit Hydrazin in alkalischer Lösung zu Nitriten reduziert werden. Die Reaktion wird durch Kupfer katalysiert. Die Autoren haben die optimalen Bedingungen für diese Reduktion festgelegt. Sie haben diese Methode verwendet, zur Bestimmung des Nitrates in Süss- und Meerwasser. Das gebildete Nitrit wird nach der Methode GRIESS-ILOSVAY bestimmt, die von MELLON UND RIDER modifiziert wurde. Die Reduktion mit Hydrazin wird ausgeführt in Anwesenheit von 0.25 p.p.m. Kupfer bei pH 9.6 in einer Natriumphenat-Pufferlösung. Sie ist quantitativ nach 24 Stunden bei gewöhnlicher Temperatur. Diese Methode erlaubt, ungefähr 0.3 μg NO_3 N/l zu bestimmen. Der Fehler ist ungefähr 2% für NO_3-N/l gehalte von 20-600 μg. Man kann 60 Bestimmungen in 6 Stunden ausführen. Der Einfluss der Nitrite wurde untersucht. Die Ammoniumsalze, der Harnstoff und die Aminosäuren stören nicht, in der vorhandenen Konzentration im Meerwasser. Vorzugsweise führt man die Analysen direkt nach der Entnahme aus, falls dies nicht möglich ist, muss das Wasser filtriert, mit 2 p.p.m. Quecksilberchlorid sterilisiert und in einem Glasbehälter konserviert werden.

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COULOMETRISCHE ARGENTOMETRIE * QUANTITATIVE BESTIMMUNG VON CHLOR-, BROM- UND JODIONEN

von

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In seinem Vortrag und im Colloquium in Genf und Bern im Mai und Juni 1952 hat TUTUNDŽIĆ[9] unter anderem auch prinzipiell neue Möglichkeiten der Anwendung der coulometrischen Titration angegeben, die in unserem Institut entweder schon ausgearbeitet waren, oder deren Ausführung im Gange war. Eine dieser Möglichkeiten, die besprochen wurde, war die Anwendung der coulometrischen Methode für quantitative Bestimmungen mittels, durch anodische Oxydation von Metallelektroden, elektrolytisch erzeugten Kathionen, die mit den zu bestimmenden Ionen schwer lösliche Verbindungen bilden.

Diese angegebene prinzipielle Möglichkeit wurde zu Methoden für coulometrische Titration von Chlor-, Brom- und Jodionen, durch elektrolytisch erzeugte Silberionen, ausgebaut. Während LINGANE UND SMALL[6] die Halogenidionen einzeln und im Gemisch, und MACNEVIN, BAKER UND MCIVER[7] im Gemisch coulometrisch durch Elektrolyse mit beschränktem Potential bestimmen, indem sie sie in Form von Silberhalogeniden in primärer Reaktion unmittelbar an der Silberanode niederschlagen und die Elektrolyse bis zu praktisch vernachlässigbarer Stromstärke führen, haben wir uns für Einzelbestimmungen von Halogeniden der coulometrischen Titration mit konstanter Stromstärke bedient, indem wir die Halogenidionen in sekundärer Reaktion als Silberhalogenide, unter Anwendung von Adsorptionsindikatoren, fällten. Unmittelbar vor der Bekanntgabe der Resultate unserer diesbezüglichen Untersuchungen im Rahmen der III Tagung der Chemiker Serbiens[11] wurde uns die Arbeit NAKANISHI's und KOBAYASHI's[8] bekannt, die zur Bestimmung von Thiocarbamid und eines Gemisches von Thiocarbamid und Rhodanid das vorher ausgeschiedene Bromion und das anwesende Rhodanidion mit elektrolytisch bei konstanter Stromstärke erzeugten Silberionen, mit potentiometrischer Endpunktsbestimmung, titrieren. Das Verfahren der erwähnten japanischen Autoren hat eine gewisse Ähnlichkeit mit unserer Arbeitsweise; der Unterschied besteht in der Art und Weise der Endpunktsbestimmung und in der technischen Ausführung. Nach der Bekanntgabe unserer Ergebnisse an der erwähnten Chemikertagung[11] erschienen die Arbeiten von LINGANE[5] und KOWALKOWSKI, KENNEDY UND FARRINGTON[4], die andere Methoden zur Ausführung der Bestimmungen von Halogenidionen durch coulometrische Titration mit konstanter Stromstärke angeben.

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Auf Grund des Studiums der Polarisationskurven der Silberanode in entsprechenden Lösungen kam BADOZ-LAMBLING[1] unlängst zum Schluss, dass die coulometrische Bestimmung von Halogeniden zwar möglich ist, sie meint aber dass, trotz glatter elektrolytischen Auflösung der Anode mit 100%-iger Stromausbeute, die coulometrische Bestimmung der Halogenide keine Vorteile im Vergleich mit der unmittelbaren amperometrischen Bestimmung biete.

Für die coulometrische Titration von Brom- und Jodionen mit konstanter Stromstärke haben wir als Grundelektrolyten eine wässrige Lösung von Kaliumnitrat angewandt, und für die coulometrische Bestimmung von Chlorionen gebrauchten wir als Grundelektrolyten eine Kaliumnitratlösung in einer Wasser-Äthanolmischung. Äthanol verringert die Löslichkeit von Silberchlorid und macht dadurch die Bestimmung von Chlorionen genauer, und ausserdem ist in Anwesenheit von Äthanol die Dispersion des niedergeschlagenen Silberchlorids grösser, wodurch die Endpunktsbestimmung mit dem gewählten Adsorptionsindikator verbessert wird. Die Konzentration der Kaliumnitratlösung als Grundelektrolyten soll so bemessen werden, dass die Reaktion zwischen Silber- und Halogenidionen durch intermediäres Gleichgewicht mit vorhandenen Nitrationen, sowie durch Diffusionswirkung, ein sekundärer Prozess wird, wobei der Elektrolytwiderstand nicht allzugross werden darf. Auf diese Weise kann erreicht werden, dass diese sekundäre Umsetzung nicht unmittelbar in der Reaktionsschicht der Anode, sondern entfernt davon, stattfindet, wodurch die Verkrustung der Silberanode und die Erhöhung des Übergangswiderstandes mit Erfolg vermieden wird. Es hat sich gezeigt, dass es am besten ist, die Konzentration von Kaliumnitrat im Grundelektrolyten zwischen 0.25 und 1*M* zu halten. Der Kathodenraum, sowie der elektrolytische Schlüssel mit Glasfritte werden ebenfalls mit entsprechender Kaliumnitratlösung, ungefähr gleicher Konzentration wie der Grundelektrolyt, gefüllt, ausgenommen bei Chlorionenbestimmungen, wobei, wegen des grossen Widerstandes des alkoholischen Grundelektrolyten, dafür eine 2*M* Lösung von Kaliumnitrat benutzt wurde. Da der Katholyt vom Anolyten durch den elektrolytischen Schlüssel getrennt ist, besteht keine Gefahr der Ausscheidung von Silberoxyd, durch sonst eintretende Erhöhung der Alkalität, als Folge der Wasserstoffabscheidung an der Platinkathode.

Der Endpunkt der Titration wird auf einfachste Weise, durch Anwendung von Farbindikatoren, und zwar von Adsorptionsindikatoren, ausgeführt. Für die Chlorionenbestimmung wurde Dichlor(R)fluorescein, und für die Bestimmung von Bromid und Jodid Eosin angewandt, worüber in der Literatur[3,2] sehr günstige Angaben vorliegen. Den vorteilhaften Einfluss von Äthanol bei der Chloridbe-

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stimmung auf die Beobachtung des Farbumschlags bei Gebrauch von Fluorescein, haben schon UZUMASA UND MIYAKE[16] bemerkt.

Die Elektrolyseneinrichtung für die coulometrische argentometrische Titration von Halogeniden besteht ebenfalls aus zwei Bechern von je 100 ml, mit entsprechenden Elektroden, verbunden durch einen elektrolytischen Schlüssel, dessen Schenkel mit Glasfrittenplättchen verschlossen sind, wie sie auch bei coulometrischer jodometrischer Thiosulfatbestimmung[12] und bei coulometrischen permanganatometrischen Bestimmungen[13,14] gebraucht wird. Als Anode dient ein Silberblech aus raffiniertem Silber mit einer Oberfläche von etwa 10 cm^3 und die Kathode bildet eine Platindrahtnetzelektrode, oder gewöhnliche Platinblech- oder Drahtspiralenelektrode. Die Stromstärke wurde mit kalibriertem Drehspulmilliampermeter der Firma Trüb, Täuber & Co — Zürich, Instrumentenklasse 0.15 gemessen, unter Anwendung der Messbereiche von 0-15 mA, 0-45 mA und 0-150 mA, und konnte durch einen Schiebewiderstand von 300 Ohm, in der Reihe mit der Elektrolysenzelle geschaltet, reguliert werden. Bei niedrigsten angewandten Stromstärken wird die Regulierung durch potentiometrische Änderung der Spannung der Gleichstromquelle über einen Widerstand von 25 Ohm bewirkt. Als Gleichstromquelle dient eine Akkumulatorenbatterie oder ein Gleichrichter mit stabilisierter Gleichstromspannung. Die maximale Stromspannung betrug 70 V. Mit der von uns verwendeten Handstoppuhr, mit einer Teilung in 0.2 sec, konnte die Zeitmessung unter unseren Arbeitsbedingungen mit einer Messgenauigkeit von 0.5 sec ausgeführt werden.

Sämtliche gebrauchten Reagentien waren „pro analysi" der Firma Merck und wurden vor Gebrauch zwei Stunden bei 110° getrocknet. Von so vorbereiteten Halogeniden wurden 0.05M und 0.01M Lösungen von KCl, 0.05M, 0.01M und 0.005M von KBr und 0.05M, 0.01M, 0.005M und 0.001M von KJ bereitet und von diesen Lösungen die benötigten Mengen durch eine kalibrierte Bürette abgemessen. Die 0.1%-ige Lösung von Dichlor(R)fluorescein in 65%-igem Äthanol wurde von einem Präparat der Firma „B.D.H." und die 0.5%-ige Lösung des Natriumsalzes von Eosin im Wasser von einem Präparat der Firma „Ciba" bereitet.

Zur Ausführung einer coulometrischen argentometrischen Bestimmung wird die Lösung mit dem zu bestimmenden Halogenid dem Grundelektrolyten geeigneter Konzentration zugegeben, so dass das Gesamtvolumen des Anolyten etwa 60 ml beträgt. Bei Bestimmungen von Bromid und Jodid wird dem Anolyten auch 1 ml 6M Essigsäure zugegeben, um die Schärfe der Endpunktsbestimmung zu verbessern. Die Stromstärke für die elektrolytische Erzeugung von Silberionen wird einerseits so eingestellt, dass die Dauer einer Bestimmung nicht mehr als 10 Minuten beträgt, was sich als sehr günstig erwies, und anderseits, hauptsächlich bei Chloriden, wird sie der Empfindlichkeit des gebrauchten Indikators angepasst. Der Anolyt wird während der ganzen Dauer der coulometrischen Titration kräftig mechanisch gerührt. Wegen der möglichen Photolyse der gebildeten Silberhalogenide wird der Anolytbehälter in schwarzes Papier eingewickelt, und die Hülle wird erst etwa zwei Minuten vor dem Titrationsende abgenommen.

Den Adsorptionsindikator gibt man erst gegen Ende der Bestimmung zu, um das Sensibilisieren der Silberhalogenide gegen Licht und den Einfluss auf die Koagulation zu vermeiden. Aus der gemessenen Zeit und konstanten Stromstärke wird mit Hilfe des Faradayschen Gesetzes die vorhandene Halogenidmenge berechnet.

Die erhaltenen Resultate zeigen die Tabellen I, II und III, die die Mittelwerte von mindestens vier Bestimmungen enthalten. In den Tabellen sind die Ergebnisse für solche ganz niedrigen Konzentrationen und kleine Mengen der Halogenide, die nach dieser Methode mit einem grösseren Fehler als 1% erzielt wurden, nicht angeführt. Absolute und relative Fehler der Bestimmungen sind durch ihre absoluten Werte ausgedrückt, und wie aus den Tabellen zu ersehen ist, sind sie meistens positiv, was auf die gewählte Endpunktsbestimmung zurückzuführen wäre.

COULOMETRISCHE CHLORIONENBESTIMMUNG

Wie aus der Tabelle I ersichtlich ist, wurde bei diesen Bestimmungen der Konzentrationsbereich der Chloride von $1 \cdot 10^{-2} M$ bis $8.3 \cdot 10^{-4} M$ erfasst. Bis zur Konzentration von $2.5 \cdot 10^{-3} M$ kann die Bestimmung des Chlorids auf die beschriebene Weise mit einem Fehler unter 0.5% ausgeführt werden. Der relative Fehler der Bestimmung beträgt bei der Konzentration von $1.7 \cdot 10^{-3} M$ etwa 0.6%, während er sich bei der Konzentration von $8.3 \cdot 10^{-4} M$ um 1% bewegt. Die kleinste

TABELLE I

COULOMETRISCHE CHLORIONENBESTIMMUNG

Den Grundelektrolyten bildet für Konzentrationen um $1.10^{-2} M$ KCl eine molare Lösung von KNO_3 in 25%-igem Äthanol, für Konzentrationen um $4.2 \cdot 10^{-3} M$ KCl eine $0.67 M$ Lösung von KNO_3 in 35%-igem Äthanol; für kleinere Konzentrationen von KCl ist der Grundelektrolyt eine $0.25 M$ Lösung von KNO_3 in 60%-igem Äthanol. Volumen des Anolyten 60 ml. Indikator: 0.1%-ige Lösung von Dichlor(R) fluorescein in 65%-igem Äthanol. Davon 4 bis 6 Tropfen je nach der Menge des abgeschiedenen Silberchlorids.

Annähernde Konzentration von KCl	Genommen Cl^-	Gefunden Cl^-	Fehler		Stromstärke	Dauer der Bestimmung
Mol/l	mg	mg	mg	%	mA	sec
$1 \cdot 10^{-2}$	21.27	21.31	0.04	0.19	100	580
$4.2 \cdot 10^{-3}$	8.86	8.90	0.04	0.45	45	538
$2.5 \cdot 10^{-3}$	5.32	5.34	0.02	0.38	30	484
$1.7 \cdot 10^{-3}$	3.55	3.57	0.02	0.56	30	324
$8.3 \cdot 10^{-4}$	1.77	1.79	0.02	1.12	23.97	203.5

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Chloridmenge die mit einem Fehler von 1% bestimmt werden kann beträgt 1.77 mg Chlorionen, wobei 4.83 Coulombs gebraucht werden. Bei diesen Bestimmungen wurden in 1 sec $2.484 \cdot 10^{-7}$ bis $1.036 \cdot 10^{-6}$ Gramäquivalente Silberionen erzeugt.

COULOMETRISCHE BROMIONENBESTIMMUNG

Bei der Bromionenbestimmung wurde der Konzentrationsbereich der Bromide von $1 \cdot 10^{-2} M$ bis $2.5 \cdot 10^{-4} M$ in Betracht gezogen (Tabelle II). Bis zu der Konzentration von $8.3 \cdot 10^{-4} M$ kann das Bromid nach der beschriebenen Arbeitsweise mit einem Fehler unter 0.25% bestimmt werden, während man bei Konzentrationen von $4.2 \cdot 10^{-4} M$ und $2.5 \cdot 10^{-4} M$ einen Fehler von etwa 0.5%, bezw. von 0.8% erreicht. Die kleinste mit einem Fehler von etwa 1% bestimmte Bromionenmenge beträgt 1.20 mg, wobei 1.45 Coulombs verbraucht werden. Die Erzeugung von Silberionen in 1 sec bewegte sich dabei zwischen $8.287 \cdot 10^{-8}$ bis $1.036 \cdot 10^{-6}$ Gramäquivalenten.

TABELLE II

COULOMETRISCHE BROMIONENBESTIMMUNG

Den Grundelektrolyten bildet für Konzentrationen um $1.10^{-2} M$ KBr eine molare Lösung von KNO_3, für Bromidkonzentrationen um $10^{-3} M$ eine $0.5 M$ Lösung von KNO_3 und für Bromidkonzentrationen um $10^{-4} M$ eine $0.33 M$ Lösung von KNO_3. Volumen des Anolyten: 60 ml. Indikator: 0.5%-ige wässrige Lösung des Natriumsalzes von Eosin. Davon 1 bis 3 Tropfen je nach der Menge des abgeschiedenen Silberbromids.

Annähernde Konzentration von KBr	Genommen Br^-	Gefunden Br^-	Fehler		Stromstärke	Dauer der Bestimmung
Mol/l	mg	mg	mg	%	mA	sec
1.10^{-2}	47.95	48.03	0.08	0.17	100	580
$4.2 \cdot 10^{-3}$	19.98	20.01	0.03	0.15	45	537
$2.5 \cdot 10^{-3}$	11.99	12.00	0.01	0.08	30	483
$1.7 \cdot 10^{-3}$	7.99	8.00	0.01	0.12	21	460
$8.3 \cdot 10^{-4}$	4.00	3.99	0.01	0.25	10	482
$4.2 \cdot 10^{-4}$	2.00	2.01	0.01	0.50	10	243
$2.5 \cdot 10^{-4}$	1.20	1.21	0.01	0.83	7.99	183.5

COULOMETRISCHE JODIONENBESTIMMUNG

Die Tabelle III zeigt, dass bei der Jodidbestimmung der Konzentrationsbereich von $1 \cdot 10^{-2} M$ bis $1 \cdot 10^{-4} M$ erfasst werden konnte. Bis zu der Konzentration von $4.2 \cdot 10^{-4} M$ kann Jodid mit einem Fehler von 0.3% bestimmt werden, während

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TABELLE III

COULOMETRISCHE JODIONENBESTIMMUNG

Den Grundelektrolyten bildet für Konzentrationen um $1.10^{-2}M$ KJ eine molare Lösung von KNO_3. für Jodidkonzentrationen um $10^{-3}M$ eine $0.5M$ Lösung von KNO_3 und für Jodidkonzentrationen um $10^{-4}M$ eine $0.33M$ Lösung von KNO_3. Volumen des Anolyten: 60 ml. Indikator: 0.5%-ige wässrige Lösung des Natriumsalzes von Eosin. Davon 1 bis 3 Tropfen je nach der Menge des abgeschiedenen Silberjodids.

Annähernde Konzentration von KJ	Genommen J^-	Gefunden J^-	Fehler		Stromstärke	Dauer der Bestimmung
Mol/l	mg	mg	mg	%	mA	sec
1.10^{-2}	76.15	76.28	0.13	0.17	100	580
$4.2\cdot10^{-3}$	31.73	31.69	0.04	0.13	45	535.5
$2.5\cdot10^{-3}$	19.04	18.98	0.06	0.31	30	481.5
$1.7\cdot10^{-3}$	12.69	12.71	0.02	0.16	21	460
$8.3\cdot10^{-4}$	6.35	6.33	0.02	0.31	10	481
$4.2\cdot10^{-4}$	3.17	3.16	0.01	0.31	6	400.5
$2.0\cdot10^{-4}$	1.52	1.53	0.01	0.66	5	232.5
$1.0\cdot10^{-4}$	0.76	0.77	0.01	1.30	4	146

bei Konzentrationen von $2\cdot10^{-4}M$ und $1\cdot10^{-4}M$ mit einem Fehler bis 1% gearbeitet werden kann. Mit diesem Fehler von etwa 1% konnte noch die Menge von 0.76 mg Jodionen mit 0.58 Coulombs bestimmt werden. Die Silberionen wurden dabei elektrolytisch in Mengen von $4.146\cdot10^{-8}$ bis $1.036\cdot10^{-6}$ Grammäquivalenten in 1 sec erzeugt.

Die erzielten Ergebnisse zeigen, dass die coulometrische Bestimmung von Halogeniden durch elektrolytisch erzeugte Silberionen, bei konstanter Stromstärke, mit der beschriebenen einfachen Apparatur, durch Endpunktsbestimmung mit den angegebenen Adsorptionsindikatoren, eine sichere und bequeme Methode für Semimikro- und Mikrobestimmungen von Halogeniden, im untersuchten Konzentrationsbereich und mit angegebenen Halogenidmengen, darstellt. Zu gleicher Zeit stellt diese Arbeitsweise auch noch eine sichere und vollentwickelte Methode dar, die im Sinne des Vorschlags von TUTUNDŽIĆ[10] an die Internationale Union für reine und angewandte Chemie[15] für die coulometrische Eichung volumetrischer Lösungen geeignet ist und für die Einführung des Coulombs als Ursubstanz in die gesamte analytische Chemie eine neue Stütze bringt. Darin besteht, trotz gegensätzlichen Meinungen[1], zweifellos auch einer der Vorzüge der coulometrischen Titration der Halogenide gegenüber der unmittelbaren amperometrischen Bestimmung.

Um die Genauigkeit der coulometrischen Bestimmung der Halogenide noch zu erhöhen, sollte auch die Anwendung objektiver und empfindlicherer Methoden für die Endpunktsbestimmung, wie z.B. der Amperometrie, studiert werden, was

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mit automatischem und noch sichererem Konstanthalten der Stromstärke zu noch grösserer Empfindlichkeit und Genauigkeit führen könnte. Nach der Veröffentlichung unserer Ergebnisse im Rahmen der erwähnten Tagung[11], gaben KOWALKOWSKI, KENNEDY UND FARRINGTON[4] ihre coulometrische Titration der Jodide mit elektrolytisch erzeugten Silberionen mit konstanter Stromstärke und amperometrischer Endpunktsbestimmung bekannt.

Coulometrische Titration mit elektrolytisch erzeugten Silberionen mit konstanter Stromstärke unter Anwendung geeigneter Adsorptionsindikatoren kann auch für die Bestimmung der Gesamtmenge der Halogenide benutzt werden, und zwar von Chlor- und Jodionen, oder Chlor- und Bromionen oder aller drei Halogenide durch Anwendung von Dichlor(R)fluorescein, während Jod- und Bromionen unter Anwendung von Eosin bestimmt werden können. Was die Bestimmung von einem Halogenid in Anwesenheit von anderen betrifft, so könnte unserer Erfahrung nach, unter Anwendung der bis jetzt bekannten Adsorptionsindikatoren, wahrscheinlich nur die Bestimmung von Jodid neben Chlorid verwirklicht werden, und zwar nur unter bestimmten Bedingungen der Stromstärke und der Zusammensetzung des Grundelektrolyten. Bis dahin, stellen zurzeit die besten Arbeitsmethoden für coulometrische Bestimmungen eines Halogenids in Anwesenheit der anderen die Methode von LINGANE UND SMALL[6] und die sogenannte coulogravimetrische Methode von MACNEVIN, BAKER UND MCIVER[7] dar.

Zum Schluss verweisen wir auf die Möglichkeit der Verwendung der, durch elektrolytische Oxydation der Silberanode, erzeugten Silberionen für die coulometrische quantitative Bestimmung auch anderer Ionen, die mit Silberionen schwerlösliche Verbindungen bilden.

ZUSAMMENFASSUNG

Durch elektrolytische Oxydation der Anoden aus verschiedenen Metallen können die Ionen des Anodenmetalls quantitativ in Lösung übergeführt werden, ein Vorgang der für die coulometrische Bestimmung anwesender Anionen, die schwerlösliche Verbindungen mit Metallionen bilden, ausgenutzt werden kann.

Es wurden Semimikro- und Mikrobestimmungen von Chlor-, Brom- und Jodionen durch elektrolytisch erzeugte Silberionen bei konstanter Stromstärke und mit einfacher Apparatur ausgeführt. Die Endpunktsbestimmung erfolgte mittels Adsorptionsindikatoren, und zwar mit Dichlor(R)fluorescein bei Chloriden und mit Eosin bei Bromiden und Jodiden. Die untere Konzentrationsgrenze der Verwendbarkeit dieser Methode ist wesentlich durch die Empfindlichkeit der gewählten Endpunktsbestimmungsmethode bedingt.

Die entwickelte Methode der coulometrischen Argentometrie stellt noch eine Möglichkeit dar für die coulometrische Eichung volumetrischer Lösungen, im Sinne unseres schon früher erfolgten Vorschlags, sowie noch eine Stütze für die Einführung des Coulombs als Ursubstanz in die gesamte Analytische Chemie.

SUMMARY

By electrolytic oxidation of various metal anodes, metal ions can be quantitatively introduced into solution. This process can be used for coulometric determination of anions forming insoluble salts with metal ions.

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Semimicro and micro determinations of chloride, bromide and iodide ions with electrolytically generated silver ions have been performed at constant current and by a simple apparatus. The end-points have been determined with adsorption indicators, *i.e.* with dichloro(R)fluorescein for chlorides and eosin for bromides and iodides. The lower concentration limit of applicability of this method depends on the sensitivity of the end-point determination method used.

The developed method of coulometric argentometry presents a new possibility for coulometric standardization of volumetric solutions, in conformity with our earlier proposals, as well as a further support for the introduction of the coulomb as a primary standard in all analytical chemistry.

RÉSUMÉ

Par oxydation électrolytique de diverses anodes métalliques, des ions formés peuvent entrer quantitativement en solution; ce processus permet de doser coulométriquement les anions formant des composés insolubles avec ces ions métalliques libérés. Il est possible d'effectuer ainsi des semimicro- et microdosages d'ions chlorhydrique, bromhydrique et iodhydrique en utilisant une électrode d'argent, et en travaillant à intensité constante. L'appareillage est simple. Le point d'équivalence est déterminé à l'aide d'indicateurs d'adsorption: la dichloro-R fluorescéine pour les chlorures et l'éosine pour les bromures et iodures. La sensibilité de ces dosages dépend de la méthode choisie pour la détermination du point d'équivalence. Cette méthode d'argentométrie coulométrique apporte une possibilité de plus pour l'étalonnage des solutions volumétriques et un argument supplémentaire pour l'introduction du coulomb dans toute la chimie analytique.

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m-NITROPHENYLARSONIC ACID AS A POLAROGRAPHIC REAGENT FOR TITANIUM

by

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This paper is concerned with a new polarographic method for titanium and with its application to the determination of this element in high temperature alloys. The method makes use of the facts that *m*-nitrophenylarsonic acid is polarographically reducible, and is a selective precipitant for titanium. Of the several elements present in the high temperature alloys studied, only iron and titanium precipitate with this reagent. Iron is conveniently removed by electrolysis of a perchloric acid solution of the alloy in a mercury cathode cell, and the titanium is then precipitated as the *m*-nitrophenylarsonate under controlled conditions. The filtered precipitate is dissolved, and the concentration of *m*-nitrophenylarsonic acid in the solution is determined polarographically. The diffusion current given by the organic reagent is related to the titanium concentration in the original solution by appropriate calibration procedures.

m-Nitrophenylarsonic acid has been little used as an analytical reagent. It was recommended some years ago for the detection of zirconium and of tin,[1,2] but its first application in quantitative analysis appears to be that proposed recently by KOLTHOFF AND JOHNSON[3]. These authors studied *m*-nitrophenylarsonic acid as a precipitant in amperometric titrations, and proposed amperometric methods for Th^{+4}, UO_2^{+2}, Zr^{+4}, and Sn^{+4}, using this reagent. They did not, however, find the reagent suitable for the determination of titanium, because of lack of constancy of composition of the precipitate under the conditions imposed by amperometric titrations[4]. We have found that *m*-nitrophenylarsonic acid will quantitatively give with titanium a precipitate of constant composition under conditions that are feasible for a polarographic method.

Polarographic reductions of titanium complexes have been carried out in media containing one or other of oxalic, citric, tartaric, or ethylenediaminetetraacetic acids[5,6,7]. Based on such reductions, mainly in tartaric acid media, there have been developed methods for the direct polarographic determination of titanium in minerals, several alloys, and other substances. These are summarized and described elsewhere[8,9,10]. Modern high temperature alloys contain such a variety of elements in substantial concentrations that, in order to avoid interferences, it is desirable that titanium be isolated before being determined. In the method described below, *m*-nitrophenylarsonic acid is used both to isolate the titanium and to determine it.

APPARATUS AND REAGENTS

Apparatus

All polarographic measurements were carried out at 25.0° C ± 0.05° C using a Tinsley polarograph, type V 722/13 (Tinsley Industrial Instruments, London, England). The capillary for the dropping mercury electrode was a length of marine barometer tubing supplied by E. H. Sargent and Co. (Chicago, U.S.A.). A conventional "H" type of polarographic cell[11] was employed, electrolytic contact to the saturated calomel reference cell being made by a potassium chloride-agar bridge.

Measurements of pH were made with a Beckman Model G pH meter, (Beckman Instruments Inc., South Pasadena, U.S.A.) using a G 1190-80 glass electrode and a saturated calomel reference electrode. A Coleman Universal Spectrophotometer Model 11, (Coleman Electric Co., Maywood, U.S.A.) was used for the colorimetric measurements.

The mercury cathode cell was of a type previously described[9].

Reagents

The *m*-nitrophenylarsonic acid was Eastman Grade obtained from Distillation Products Industries (Rochester, U.S.A.). This was dissolved in water to make a 0.8 % solution. The solution was adjusted to a pH of 1.2 with concentrated perchloric acid, and, after standing for 24 hours at room temperature, was filtered to remove any insoluble material.

Tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate) for the colorimetric work was supplied by the La Motte Chemical Products Company (Baltimore, U.S.A.).

A 1 % gelatin solution, used to suppress polarographic maxima when methyl red was not present in the solution, was prepared from Eastman Kodak Pigskin Gelatin (Eastman Kodak Company, Rochester, U.S.A.).

Mercury for the mercury cathode cell and the dropping mercury electrode was purified by bubbling for at least 10 hours with 10-15% nitric acid, washed several times with water, and then distilled twice *in vacuo*.

Two stock solutions were used as sources of titanium during the study of the factors influencing the precipitation of titanium as the *m*-nitrophenylarsonate. Stock solution #1 was prepared by dissolving 0.83 g of titanium dioxide (Standard #154 of the National Bureau of Standards, Washington, U.S.A.) in 5.0 ml of boiling 18*M* sulfuric acid containing 3.0 g of ammonium sulfate. After cooling, the material was added to 300 ml of $1.7M$ perchloric acid. The sulfate was removed by precipitation with barium chloride and filtration. The filtrate was diluted to 500 ml with a perchloric acid solution of pH 1.2, giving a concentration of titanium of 1 mg per ml. Stock solution #2 was prepared by dissolving 12 g of a Discaloy alloy in perchloric acid in a manner similar to that described under PROCEDURE, below. Small samples were then electrolyzed in the mercury cathode cell until a spot test for iron with thiocyanate was negative. The electrolyzed samples were added together to make 250 ml of solution, the concentration of titanium being 0.8 mg per ml.

All other chemicals were analysed grade.

"Tartrate solution" was prepared by making a $0.5M$ solution of tartaric acid strongly alkaline to phenolphthalein with concentrated sodium hydroxide. "Wash liquid" was an aqueous solution of perchloric acid of pH 1.2.

VARIABLES INFLUENCING PRECIPITATION

A careful study was made of the variables influencing the quantitative precipitation of titanium with *m*-nitrophenylarsonic acid; pH, concentration and nature of anions present, concentration of titanium and of reagent, and coagulation procedures.

pH

The extent and nature of the precipitation of titanium by *m*-nitrophenylarsonic acid depends on the pH of the medium. At low pH values, no precipitation occurs, whereas at relatively high pH values the titanium is precipitated mainly as the hydrous oxide; only at intermediate pH values is the precipitation of titanium as the *m*-nitrophenylarsonate accomplished quantitatively.

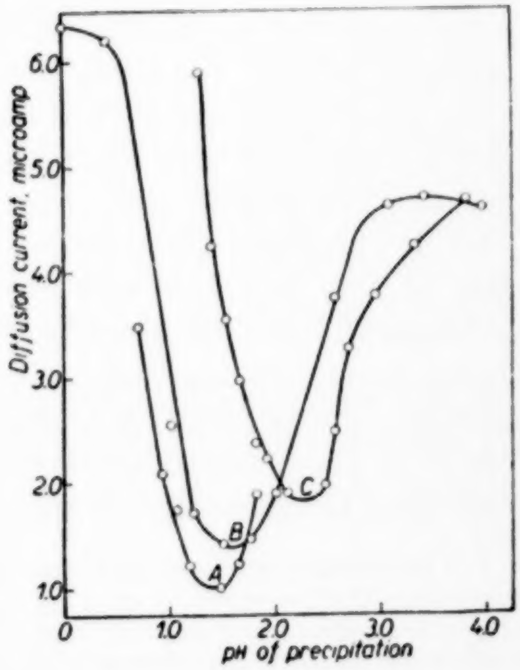

Fig. 1. Effectiveness of *m*-nitrophenylarsonic acid as a precipitant for titanium as a function of pH and concentration of sulfate. In the experiments represented by Curve A, the concentration of sulfate was $1.1\cdot10^{-3}M$; by Curve B, $4.1\cdot10^{-3}M$; and by Curve C, $3.6\cdot10^{-2}M$.

Curves relating the extent of precipitation to the pH of precipitation were constructed as shown in Fig. 1. Each point on these curves was obtained by adding to 5.00 ml of stock solution #1 sufficient sulfuric acid to give (in the final volume of 110 ml) the sulfate concentration stated in the caption of the Figure, then water to give a volume of 100 ml, and then 10.00 ml of 0.8% *m*-nitrophenylarsonic acid solution. Both the *m*-nitrophenylarsonic acid solution and the diluted titanium solution were separately adjusted to the same desired pH, using 7.5*M* ammonia or 2.5*M* perchloric acid, before being brought together. The white precipitate produced on mixing was digested for one hour at room temperature and the pH of the mixture then determined. The pH values plotted are, in each case, the mean of the two values, which differed by 0.1 pH units or less. The precipitate was filtered, washed with wash liquid and the filtrate and washings together adjusted to a pH of 4.0 with 7.5*M* ammonia. The solution was then buffered with 50 ml of a 0.50*M* solution of potassium hydrogen phthalate, brought to a total volume of 250 ml with water and polarographed. The diffusion current corresponded to the concentration of unreacted *m*-nitrophenylarsonic acid, and thus was an indication of the composition of the precipitate.

The lowest points on the curves correspond to the pH values at which titanium is precipitated essentially completely as the *m*-nitrophenylarsonate.* Only this pH region is of interest in this work and hereafter is referred to as optimum pH. Points on the curves at lower pH values correspond to incomplete precipitation of titanium; at pH values higher than the optimum, the precipitation of titanium is quantitative, but hydrous oxide as well as arsonate is precipitating.

Nature and concentration of anions

Although, at the optimum pH, the titanium was quantitatively precipitated in the experiments summarized in Fig. 1, it is evident that the lower the concentration of sulfate, the more complete is the precipitation and the lower is the pH at which it occurs. Both these observations are consistent with the fact that sulfate complexes with titanium. It is accordingly desirable to precipitate the titanium in solutions free of sulfate.

When perchloric acid replaced sulfuric acid as the dissolving medium for the alloy, it was found, as was expected from the lesser tendency of perchlorate to complex[6], that the titanium was more readily precipitated. In the procedure finally developed, the only anion present at the time of precipitation was perchlorate. It was found, too, that the range of optimum pH was wider, *i.e.*, the trough of the precipitation curve was shallower, in the absence of sulfate. The conditions recommended below under PROCEDURE permit a variation of ± 0.4

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* The filtrate was tested colorimetrically for unprecipitated titanium using Tiron according to the method of YOE AND ARMSTRONG[12]. It was found that at pH values in the troughs of the curves, and at higher pH values, 99.9% or more of the titanium originally present had been precipitated.

pH units from an optimum value of 1.2 while still achieving a precipitation of titanium that is at least 99.9% complete (as shown by colorimetric tests on the filtrate).

Concentration of reagent

Although titanium can be precipitated quantitatively with a modest excess of *m*-nitrophenylarsonic acid, a substantial excess was found necessary for the precipitate to be of constant composition. Diluted portions of stock solution #2 containing 4 mg of titanium were precipitated at a pH of 1.2 with increasing amounts of *m*-nitrophenylarsonic acid, (from 5 to 75 ml of the reagent solution); in these experiments the ratio of moles of reagent to moles of titanium varied from about 2:1 to 30:1. The amount of organic reagent in the precipitate was found by filtering it, washing with wash liquid, dissolving it in tartrate solution, and then polarographically determining the concentration of *m*-nitrophenylarsonic acid in the solution. A curve relating the amount of organic reagent in the precipitate to volume of precipitating solution rose until 30 ml of reagent had been used and then became constant. For the 4.0 mg of titanium present, this corresponded to a ratio of about 10 moles of reagent to 1 of titanium. Colorimetric tests on the filtrate showed that 99.9 % or more of the titanium had been precipitated; in fact the precipitation of titanium was quantitative when the excess of reagent was much less than that required to give a precipitate of constant composition.

Concentration of titanium

In a study of the minimum concentration of titanium that could readily be determined, solutions containing from 0.5 to 50 mg/l (prepared from stock solution #2) were precipitated at a pH of 1.2 with graduated amounts of *m*-nitrophenylarsonic acid solution so that from a 12- to 36-fold excess of reagent was present in all cases. The titanium in the precipitate was assessed from the polarographic diffusion current given by the *m*-nitrophenylarsonic acid obtained by dissolving the precipitate in the manner described earlier. It was found that for concentrations of titanium less than 10 mg/l (before the addition of the precipitating solution) solubility losses prevented quantitative recovery of the titanium. If the solution contains much above 4.0 mg of titanium, the voluminous precipitate is not conveniently manipulated.

Losses may also be experienced due to the ease with which titanium is hydrolyzed and because the *m*-nitrophenylarsonate precipitate is readily peptized. For these reasons all washing operations were carried out using an acid solution (perchloric acid of pH 1.2).

Heating of precipitate

The addition of the reagent to the titanium solution resulted in the immediate

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formation of a finely divided precipitate. This coagulated nicely within one hour on digestion at room temperature, but much more rapidly at 90° C. It was found, however, that the composition of the precipitate digested at the higher temperature was not constant, even in the presence of a 30-fold excess of reagent.

POLAROGRAPHY OF *m*-NITROPHENYLARSONIC ACID

Low concentrations of *m*-nitrophenylarsonic acid are easily detected polarographically, the type of wave obtained being shown in Fig. 2. The height of the wave, or the diffusion current, can be easily measured with good precision. The wave corresponds to the reduction of the nitro group at the dropping mercury electrode in a solution buffered at a pH of 4.0 with $0.15M$ potassium hydrogen phthalate. Although *m*-nitrophenylarsonic acid can give three reduction waves, only one appears at a pH of 4; this probably corresponds to the reduction of the nitro compound to a phenylhydroxylamine[3]. Because the diffusion current given by the organic compound can be expected to vary with pH[13], a good buffer is required to ensure analytically useful results. Potassium hydrogen phthalate at a concentration of $0.15M$ serves well both as a buffer and as a supporting electrolyte. When methyl red is also present in the solution, as it is in the recommended procedure, polarographic maxima are not observed. The diffusion current given by the *m*-nitrophenylarsonic acid is linearly related to the amount of titanium in the original solution, as shown in Fig. 3.

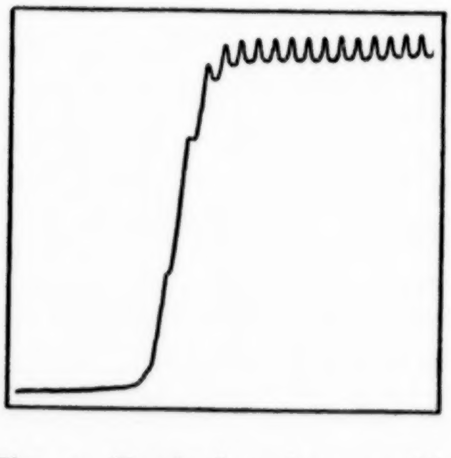

Fig. 2. Typical polarographic wave for the reduction of *m*-nitrophenylarsonic acid.

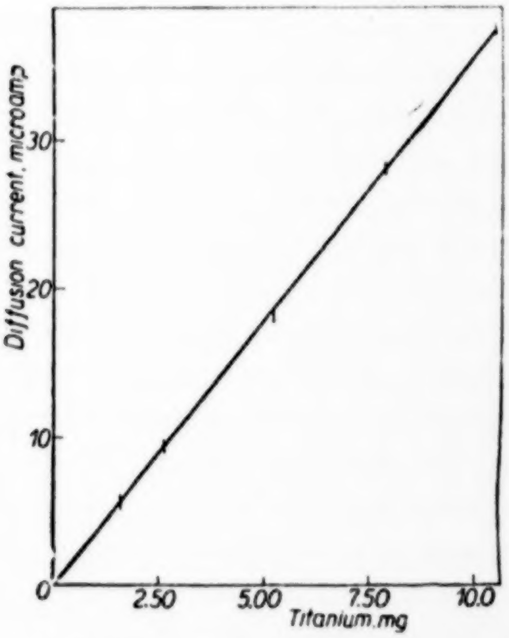

Fig. 3. Diffusion current of *m*-nitrophenylarsonic acid as a linear function of the amount of titanium present in the solution from which it was precipitated.

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PROCEDURE AND RESULTS

A 1.2 to 2.0 g sample of alloy turnings (containing about 2 % titanium) is accurately weighed, placed in a 250 ml round-bottomed standard taper flask, and covered with 40 ml of 72 % perchloric acid. A reflux condenser is attached to the flask, and the whole inclined at an angle of 60° to the horizontal. The contents of the flask are heated to boiling, whereupon the alloy is readily attacked. Heating is continued until all of the metal has dissolved, leaving only a white siliceous residue.

The contents of the flask are quantitatively transferred to a 250 ml volumetric flask, and made up to the mark (with wash liquid). A 25 ml aliquot sample of the solution is transferred to a mercury cathode cell, diluted to about 70 ml with wash liquid, and electrolyzed (at a current density of 0.15 amp./cm^2 and 5 volts) until a negative spot test for iron using thiocyanate is obtained. (This in general requires about half an hour). The solution is then transferred to a 250 ml beaker and adjusted to the optimum pH of 1.2 ± 0.4 with 7.5 M aqueous ammonia. At this point the total volume of solution is about 150 ml. Fifty ml of the aqueous reagent solution are then added, resulting in the formation of a precipitate.

The precipitate is digested at room temperature for one hour, and is then filtered on Whatman #42 paper, washed three times with wash liquid, and dissolved by adding dropwise 6 ml of a near-boiling tartrate solution. The solution is caught in a 100 ml volumetric flask and adjusted to the methyl red end-point with 5M perchloric acid. Thirty ml of 0.50M potassium hydrogen phthalate are added, and the solution is brought up to the mark with distilled water. The solution is deaerated by bubbling with purified nitrogen, and is polarographed at a counter current setting of 0, a galvanometer sensitivity of 20 microamp per full scale deflection, and a damping setting of 2. Four waves are recorded for each solution and the average wave-height, measured by the slope intercept method, is calculated.

For calibration purposes a standard alloy sample (Inconel W) was analysed with each batch of alloy samples under test. The titanium content of the standard alloy (2.32 %) had been established by analyses of umpire grade carried out by the manufacturer, and subsequently satisfactorily confirmed by an independent polarographic method[9]. The titanium contents of the original solutions of the alloys under test were assessed by comparing the diffusion currents with that given by the solution from the standard alloy. This procedure eliminates the effect of day-to-day variations in instrumentation.

The method was applied to several different high temperature alloys, with the results shown in Table I.

DISCUSSION

The "standard" values listed in Table I were obtained, in the laboratories of

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TABLE I

RESULTS OF ANALYSES

Alloy	Polarographic Individual			Average	Standard value
Company A					
A-286	1.94	1.92	1.93	1.93	1.92
Waspalloy	2.26	2.26	2.21	2.24	2.27
Discaloy 1	2.15	2.08	2.12	2.12	2.09
Company B					
Discaloy 2	1.74	1.71	1.67	1.71	1.71
Discaloy 3	1.67	1.65	1.66	1.66	1.66
Company C					
Inconel X	2.36	2.36	2.36	2.36	2.43
Company D					
K42B 131	2.81	2.86	2.91	2.86*	2.85
K42B 601	2.22	2.22	2.20	2.21*	2.23

* In these analyses a standard Discaloy sample supplied by Company D was used for calibration purposes. For all other analyses a standard sample of Inconel W was used.

the companies that kindly supplied the samples, by colorimetric and gravimetric methods of an umpire grade. The accuracy of the polarographic method in all but one case is very good and the precision is as good or better than can be expected when applying a polarographic method at the 2 % level. Table II shows both the complexity of the alloys and the widely differing compositions to which the method is applicable.

In analyses of the two samples of K42B alloy and a sample of Discaloy of Company D, the polarographic results were all distinctly low (but "correct" proportionately to one another) when the standard Inconel W alloy was used for calibration. When the K42B samples were analysed using the Discaloy sample of the same company as a standard, the polarographic values were in very good agreement with the company's "standard" values, as shown in Table I. We

TABLE II

AVERAGE PERCENTAGE COMPOSITION OF ALLOYS

Element	Discaloy	K42B	Waspalloy	Inconel X*	A-286
Iron	53	13	3	7	53
Nickel	26	41	57	72	26
Chromium	14	19	19	15	15
Cobalt	—	22	14	—	—
Molybdenum	3.2	—	3.1	—	1.2
Titanium	1.8	2.5	2.3	2.4	1.9
Manganese	0.7	0.9	0.8	0.7	1.4
Silicon	0.8	0.7	0.6	0.4	0.9
Aluminium	0.1	0.5	1.1	1.0	0.2
Vanadium	0.08	0.05	—	—	0.3
Carbon	0.04	0.04	0.05	0.04	0.03

* Also contains Cu, 0.1%; Cb, 0.7%; and Ta, 0.2%.

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believe that there is a systematic error in the analyses of Company D. Not only have Discaloy samples from two other companies been successfully analysed by the polarographic method but also, as noted below, the composition of the precipitate would be anomalous if the analyses of Company D were accepted.

By constructing a calibration curve relating the concentration of *m*-nitrophenylarsonic acid* to its diffusion current, the number of moles of the reagent associated in the precipitate with one mole of titanium could be calculated. Using the "standard" values given by companies other than Company D this number was 2.0, indicating that the precipitate was a diarsonate. The "standard" values of Company D led to the curious ratio of 1.7 whereas our values for the alloys of Company D, based on a calibration using Inconel W, yielded the ratio 2.0.

The determination of titanium by this method is very convenient when the concentration of the solution to which the reagent solution is added is about 20 mg/l or 20 p.p.m., but it can be used with concentrations only half this without significant solubility losses. This sensitivity compares favourably with that of the colorimetric method using hydrogen peroxide[15,16,17], and the polarographic method appears to be less subject to interferences than either this colorimetric method or the one using Tiron[12]. In general, Fe^{+3}, Sn^{+4}, Zr^{+4}, Th^{+4}, Bi^{+3}, and UO_2^{+2} are precipitated by *m*-nitrophenylarsonic acid; although tin and bismuth are not present in the high temperature alloys to which we have applied the method, these can be removed with iron by an electrolysis in a mercury cathode cell.

m-Nitrophenylarsonic acid is not attractive as a reagent for the gravimetric determination of titanium. With amounts of titanium that are sufficiently large for gravimetric work, the precipitate is bulky and difficult to wash. Drying of the precipitate at 105-110° C yields a hygroscopic substance, and ignition is liable to entail losses due to the explosion of the nitro compound.

ACKOWLEDGEMENTS

Grateful acknowledgement is made to the Research Council of Ontario and to the Defence Research Board of Canada for financial support. Thanks are also due to Mr. A. HITCHEN (Department of Mines and Technical Surveys, Ottawa, Canada) who, when in this laboratory, aroused our interest in the organic reagent used, and, since leaving it, has maintained a helpful interest in the work.

SUMMARY

A sensitive polarographic method for titanium, based on its selective and quantitative precipitation with polarographically reducible *m*-nitrophenylarsonic acid is described. Factors affecting the quantitative precipitation — pH, concentration, of titanium and reagent, nature and concentration of anions, and digestion — have been studied.

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* For this purpose the reagent was recrystallized by the method given in *Organic Syntheses*[14].

After precipitation of the titanium under controlled conditions, the precipitate is dissolved and the polarographic diffusion current of the organic reagent is related, by a calibration, to the original titanium concentration.

The method has been applied successfully to the determination of titanium in complex high temperature alloys, after the removal of iron by a mercury cathode electrolysis.

RÉSUMÉ

Les auteurs décrivent une méthode de dosage sensible du titane, basée sur sa précipitation sélective et quantitative au moyen de l'acide *m*-nitrophénylarsonique (réactif réductible polarographiquement). Les facteurs influençant cette précipitation (pH, concentration du titane et du réactif, nature et concentration des anions, digestion) ont été étudiés. Après précipitation du titane dans des conditions déterminées, le précipité est dissous. La teneur en titane est alors déterminée à partir de la quantité de réactif mesurée polarographiquement. Cette méthode a été utilisée avec succès pour le dosage du titane dans les alliages complexes, après élimination du fer par électrolyse, à la cathode de mercure.

ZUSAMMENFASSUNG

Die Autoren beschreiben eine empfindliche Methode für die Bestimmung von Titan, welche auf seiner selektiven und quantitativen Ausfällung mit Hilfe von *m*-Nitrophenylarsonsäure (polarographisch reduzierbares Reaktiv) beruht. Die diese Ausfällung beeinflussenden Faktoren (pH, Konzentration des Titans und des Reaktivs, Art und Konzentration der Anionen) wurden untersucht. Nach der Ausfällung des Titans unter diesen bestimmten Bedingungen wird der Niederschlag aufgelöst. Der Gehalt an Titan wird also mit Hilfe der polarographisch gemessenen Quantität des Reaktivs bestimmt. Diese Methode wurde mit Erfolg angewendet für die Bestimmung von Titan in komplexen Legierungen nach einer elektrolytischen Abscheidung des Eisens an der Quecksilberkathode.

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REVUE DE LIVRES

New Instrumental Methods in Electrochemistry par PAUL DELAHAY, Interscience Publishers, Inc., New York, 1954, 437 pages + figures, $ 11.50.

Jusqu'à une époque toute récente encore, la nature des phénomènes intervenant au voisinage d'une électrode et déterminant les potentiels pris par celle-ci en fonction de la composition de la solution, n'intéressait qu'un nombre extrêmement limité de chimistes. La classique théorie de NERNST appliquée aux conditions particulières de l'électrochimie, satisfaisait les vagues curiosités de praticiens considérant la question somme toute d'assez loin.

Depuis lors, au fur et à mesure que se développaient les nombreuses méthodes d'analyse et de contrôle, basées sur les propriétés électrochimiques des solutions, des divergences apparurent entre les valeurs prévues par la théorie et les résultats expérimentaux. La solution de facilité consista à enregistrer les faits en attribuant un caractère d'irréversibilité — terme extrêmement vague en électrochimie — aux processus conduisant à des résultats aberrants.

Quelques chercheurs soulignèrent cependant l'illogisme qu'il y avait à analyser, au moyen de conceptions d'équilibre statique, des phénomènes essentiellement dynamiques; d'autres insistèrent sur la nature hétérogène du milieu réactionnel. Ce fut le point de départ de quelques écoles qui s'attachèrent à l'étude de la cinétique et du mécanisme des réactions sur les électrodes, et amenèrent de très grands progrès dans la compréhension de ces phénomènes.

Les résultats de ces travaux qui intéressent aujourd'hui la plupart des chimistes — ils sont plus ou moins indispensables à une utilisation correcte des méthodes électrochimiques de contrôle —étaient malheureusement dispersés dans la littérature.

Le Dr. DELAHAY, qui tint incontestablement une des toutes premières places dans le développement de ces recherches, était particulièrement compétent pour en faire la synthèse: il la met avec ce livre, à la portée de tous. Divisé en quatre partie, l'ouvrage traite des sujets suivants:

1ère partie: Formulation mathématique, cinétique des réactions sur l'électrode, transfert de matière entre la solution et l'électrode, étudiés théoriquement en fonction des conditions d'utilisation: potentiométrie à courant nul ou constant, mesures à potentiel constant, variable ou périodique, polarographie, etc.

2ème partie: Coulométrie à courant et à potentiel constants, séparations électrolytiques et questions annexes.

3ème partie: due à la plume de CHARLES N. REILLEY, cette partie est consacrée aux méthodes utilisant la haute fréquence.

4ème partie: Instrumentation utilisée dans tout le champ des méthodes modernes électrochimiques.

En appendice on trouve encore quelques notes sur la résolution des équations différentielles nécessaires pour exprimer la cinétique des processus aux électrodes.

G. BARBEZAT (Genève)

Mises au point de Chimie analytique pure et appliquée et d'analyse bromatologique, publiées sous la direction de J. A. GAUTIER, per M. GUILLOT, Y. RAOUL, F. PERRET, J. RENAULT, M. GUIGOZ ET S. STOLL — Masson et Cie, Paris, 1954. — 108 pages avec 1 figure et 3 planches hors-texte dont une en couleur, 16.8 × 25.5 cm, 900 fr., broché.

Cette brochure, la deuxième de la série, résume 6 conférences données en 1953 à la Faculté de Pharmacie de Paris sur des sujets touchant à l'analyse des produits alimentaires. Le Prof. GUILLOT débute avec un cours agrémenté de remarques personnelles sur la colorimétrie et le choix des appareils à utiliser, puis, le Prof. RAOUL indique les difficultés relatives à l'estimation des vitamines A, B_6, B_{12}, D, PP, l'acide pantothénique. M. PERRET fait une étude détaillée de l'analyse des boîtes à conserves et de leur contenu: viandes, poissons, lait, légumes, confitures. Après quoi, M. JEAN RENAULT critique l'emploi des ammoniums quaternaires comme conservateurs d'aliments et indique leur mode de détection, puis, M. MAURICE GUIGOZ, directeur de la Société bien connue parle des méthodes pour apprécier la valeur des laits condensés. Enfin, dans une très belle conférence, Mlle SIMONE STOLL donne quelques cas particuliers d'application de la chromatographie pour la chimie des aliments et présente les chromatogrammes donnés dans les farines par l'ergot de seigle, la nielle, le mélanpyre; elle se penche aussi sur un problème d'actualité en biscuiterie: la recherche de l'éthylvanilline dans la vanilline.

Ces articles sont très bien présentés et accompagnés d'une bibliographie choisie; le papier et les caractères sont excellents. De telles conférences sont précieuses pour les analystes qui doivent se livrer à l'essai des produits alimentaires et le Prof. GAUTIER avait bien choisi ses conférenciers.

C. DUVAL (Paris)

Analyse des matières minérales, par ALBERT MEURICE ET CHARLES MEURICE, 4ème édition. Georges Thone, Liège, 1954, 981 pages, 116 figures, prix: 975 Fr. belg. (vente en Benelux); 6825 Fr. franç. (vente hors Benelux, Editions Dunod, Paris).

Cette nouvelle édition, revue et mise à jour, a tenu compte des exigences de l'industrie: analyses toujours plus exactes, toujours plus rapides. A côté des méthodes classiques et standardisées, un certain nombre de méthodes modernes sont décrites, avec utilisation d'appareils automatiques ou semi-automatiques, et nombreux sont les dosages photocolorimétriques cités. Cet ouvrage traite des échantillonnages, de l'analyse des combustibles, eaux industrielles, calcaires, dolomies, chaux, plâtres, ciments, mortiers, bétons, argiles, minerais de fer et minerais connexes. En résumé: excellent ouvrage, facile à consulter, pouvant être recommandé comme cours et comme manuel de laboratoire.

Y. RUSCONI (Genève)

Gmelins Handbuch der Anorganischen Chemie, 8. Auflage, Verlag Chemie. G.m.b.H. Weinheim/Bergstrasse, 1954.

Faisant suite à nos comptes rendus précédents (voir *Anal. Chim. Acta*, 11 (1954) 400) nous signalons la parution de trois nouveaux fascicules de cette remarquable collection:

1. Bor 13 Ergänzungsband, 1954, VII, 253 pages, 28 fig., prix: cart. 140 DM, relié 145 DM. comprenant:
(a) état naturel; formation et préparation, propriétés physiques et chimiques, identification et dosage du bore élémentaire,
(b) description des composés du bore avec l'hydrogène, l'oxygène, l'azote, le fluor, le chlore, le brome, l'iode, le soufre, le carbone.
2. Gold 62 Lief. 2, 1954, V, 306 pages, 20 fig., prix: cart. 168 DM comprenant: état naturel, préparation, extraction, purification de l'or.
3. Gold 62 Lief. 3, 1954, XXI, 558 pages, 201 fig., prix. 312 DM comprenant:
(a) propriétés physiques, électrochimiques, chimiques, physiologiques de l'or,
(b) identification et dosage,
(c) composés de l'or (avec H, O, N, F, Cl, Br, I, S, Se, Te, C, Si, P, As, Li, Na, K, NH_4, Rb, Cs, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Th, Pb, V, Cr, Mo, W, Mn, Ni, Co, Fe, Cu, Ag),
(d) alliages de l'or.

Y. RUSCONI (Genève)

COMPLEX CITRATES OF METALS IN INORGANIC ANALYSIS

PART I. SOME PRELIMINARY OBSERVATIONS AND THE APPLICATION OF CITRATE COMPLEX FORMATION IN THE QUALITATIVE ANALYSIS OF THE METALLIC IONS OF THE SILVER GROUP

by

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In spite of considerable information available in the literature on the formation of complexes involving oxalate, malonate and tartrate ions, the work on complex citrates appears to have received scanty attention. The references on record are only of recent work, for example, on copper and nickel citrates by BOBTELSKY AND JORDAN[1], and on the citrates of copper(II), cadmium, zinc, iron(III), platinum, vanadium, uranyl and beryllium, by PARRY AND DU BOIS[2], MEITES[3] KETELLE AND BOYD[4], DEFORD AND ANDERSEN[5], FELDMAN and others[6] and by WARNER AND WEBER[7], and have all been reported only within the last decade. In previous publications from this laboratory, DEY[8] reported the formation of complex citrates by the interaction of silver ion and a soluble citrate. SUZUKI[9], in a later paper, referred to the formation of a silver citrate complex and has studied the system by the potentiometric compensation method. BOBTELSKY AND GRAUS[10] have reported a heterometric micro-determination method for the estimation of lead, employing citric acid.

We now propose to undertake a detailed study of various complex metallic citrates and in the present series of papers we shall report the application of citrate complex formation in inorganic analysis.

When a solution of sodium citrate is added to a solution of silver nitrate, a white precipitate of silver citrate appears, which dissolves in excess of the citrate, producing a colourless solution. Similar observation is made with solutions of mercurous and lead salts. Our observations, thus, suggest the formation of citrate complexes with silver, lead and mercurous ions. It is further noted, that on the addition of a soluble chloride solution to the solution of the complexes, silver and mercurous chlorides precipitate out completely, while lead chloride does not precipitate even on adding excess of chloride ions, or on boiling with a chloride solution. It has also been observed that lead chloride dissolves easily on shaking with a concentrated sodium citrate solution in the cold, whereas mercurous and silver chlorides do not dissolve.

Qualitative analysis of silver group metals

These observations can be employed to effect a separation of silver, lead and mercurous ions in qualitative analysis. The method, it must be noted here, has no particular advantage over the usual method adopted for the analysis of silver group on a macroscale, but has nevertheless been recorded here, on account of the fact, that it employs a new principle, *i.e.*, complex citrate formation. The method is presented in Table I.

TABLE I

<table>
<tr><td colspan="3"><i>Precipitates of Silver Group</i>: Chlorides of silver, lead and mercurous.
Shake with a concentrated solution of sodium citrate in cold, and filter:</td></tr>
<tr><td><i>Filtrate</i>: Lead citrate complex.
Add potassium chromate solution</td><td colspan="2"><i>Residue</i>: Chlorides of silver and mercurous.
Shake with ammonia solution in cold and filter:</td></tr>
<tr><td>Yellow precipitate of lead chromate
Lead</td><td><i>Filtrate</i>: Silver ammine complex
Acidify with dilute nitric acid
White curdy precipitate of silver chloride
Silver</td><td><i>Residue</i>: Black in colour
Mercuric amidochloride + metallic mercury
Mercurous</td></tr>
</table>

The above method has successfully been employed for the analysis of a number of artificial mixtures, even with very low concentrations of the metals.

Detection of lead when present as insoluble lead sulphate in an inorganic mixture

Lead, when present as insoluble lead sulphate in an inorganic mixture, is usually identified by treating the insoluble residue with ammonium acetate solution, in which it is only partially soluble, and identifying the lead in the solution by potassium chromate. We have now observed that lead sulphate completely dissolves in a solution of sodium citrate when heated, and thus can easily be detected in the solution by the addition of potassium chromate. It may be mentioned that barium and strontium sulphates are not soluble in sodium citrate solution and hence the detection of lead by this method necessitates no further tests.

The use of the citrate complexes in the quantitative separation of silver group metals is being attempted and some experiments have shown promise of success. The details of the procedure will be described in a further communication.

SUMMARY

The use of sodium citrate as a reagent for the separation of silver group metals has been described. Silver, lead and mercurous ions are all capable of forming soluble citrate complexes, but they differ in their stability. The lead complex is not decomposed by soluble chlorides, whereas silver and mercurous complexes yield the insoluble chlorides. The fact that lead sulphate is soluble in a hot solution of sodium citrate has been utilized for the detection of lead, when present as insoluble sulphate, in a mixture.

References p. 503.

RÉSUMÉ

Les auteurs proposent l'utilisation du citrate de sodium comme réactif de séparation des métaux du groupe de l'argent. L'argent, le plomb et le mercure(I) peuvent former un citrate complexe soluble, mais de stabilité différente. Le plomb ainsi complexé n'est pas décomposé par les chlorures solubles, tandis que l'argent et le mercure précipitent comme chlorures. Le sulfate de plomb est soluble dans des solutions bouillantes de citrate de sodium: cette propriété a été utilisée pour la détection du plomb se trouvant sous forme de sulfate insoluble dans un mélange.

ZUSAMMENFASSUNG

Die Autoren schlagen die Verwendung von Natriumcitrat vor, als Trennungsreaktiv für die Metalle der Silbergruppe. Das Silber, das Blei und das Quecksilber können lösliche Citrat-Komplexe bilden, aber mit verschiedener Stabilität. Das so komplexierte Blei wird durch lösliche Chloride nicht zersetzt, während das Silber und das Quecksilber als Chloride ausfallen. Das Bleisulfat ist löslich in siedenden Natriumcitrat-Lösungen: von dieser Eigenschaft wurde Gebrauch gemacht um das Blei nachzuweisen, welches sich als unlösliches Sulfat in einer Mischung befindet.

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VANADAMETRY
ESTIMATION OF THIOSULPHATE

by

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Thiosulphate is almost exclusively determined through iodometry. A satisfactory substitution of iodometry by other oxidation methods has not attained any considerable vogue. Oxidation of thiosulphate with potassium permanganate, potassium dichromate or ceric sulphate in acid solution yields mixtures of products, the composition of the mixture varying with the conditions of the experiment. PEAN DE ST. GILLES[1] investigated the oxidation of thiosulphate with potassium permanganate in acid solution and reported dithionate and sulphate to be the products of oxidation. DOBBIN[2] found tetrathionate also in the products. BENRATH AND RULAND[3] believed that thiosulphate could be titrated directly by ceric sulphate to the tetrathionate stage. But FURMAN AND WALLACE[4] found that the amount of ceric solution consumed in this titration exceeds the amount required for the oxidation to the tetrathionate stage. LANG AND KURTENACKER[5] reported that the excess consumption of ceric solution is about 20%.

They also stated that even exactly identical experiments give dissimilar results. JELLINEK AND WINOGRADOFF[6] tried to utilise the reaction of thiosulphate with ferric salts for the purpose. They titrated the ferric solution while hot (about 50° C) with thiosulphate solution using methylene blue-fuchsine as indicator. Near the end-point, the solution is heated to boiling and the thiosulphate dropped in carefully, until the colour changes from blue to red. KOLTHOFF AND TOMICÊK[7] have tested this method and stated that it does not give accurate results. LANG AND KURTENACKER[5] oxidized thiosulphate to the tetrathionate stage by reacting it with excess of ferric solution for 5 to 10 minutes in the presence of copper salt as catalyst. The resulting ferrous salt is estimated by titration with ceric sulphate (but not with permanganate) using ferroin as indicator up to a colour change from reddish brown to light bluish green; the error is stated to be 0.1 to 0.5%. Sulphate, dithionate, tetra and polythionate are supposed to have no influence on the results. CARRIÈRE AND DALPLA[8] have studied the comparative action of potassium iodate and periodate on acidified solution of sodium thiosulphate. MURTHY[9] reports that thiosulphate is oxidized quantitatively to sulphate by chloramine-T in acid solution at room temperature.

SECTION I

Oxidation of thiosulphate to sulphate by vanadic acid

The reaction between sodium thiosulphate and vanadic acid does not appear to have received sufficient attention. LANG AND KURTENACKER[5] found that if thiosulphate solution were allowed to flow at room temperature into an excess of $0.2N$ vanadic acid solution (containing sulphuric acid) and kept for 10 minutes, considerably more vanadic acid was consumed than required for the oxidation of the thiosulphate to tetrathionate. Hence, they discarded the reaction as being useless for volumetric analysis. In view of the paucity of literature on the subject, we have considered it fruitful to make a detailed study of the reaction between vanadic acid and sodium thiosulphate. A critical examination of the published literature on thiosulphate oxidation shows that most oxidizing agents oxidize thiosulphate first to tetrathionate, which may undergo further oxidation to sulphate if the conditions are favourable. The second reaction proceeds to varying extents so that irregular results are secured. The present investigation covers a study of the influence of acid concentration, temperature, catalyst *etc.* on the course of the reaction between vanadic acid and thiosulphate. If sodium thiosulphate is allowed to react with excess of vanadate in presence of sulphuric acid, the unreacted vanadate can be estimated by titration with standard ferrous ammonium sulphate solution, using diphenylbenzidine as indicator, provided that all the thiosulphate has disappeared. If the reaction is not completed, it is not possible to estimate the excess of vanadic acid by this method, as the indicator fails to work in the presence of unreacted thiosulphate. The failure to obtain the blue violet colour of the indicator (even though a large excess of vanadic acid is present) indicates the presence of unreacted thiosulphate and the incompleteness of the reaction. Table I incorporates the results obtained during a study of the influence of varying sulphuric acid concentration.

TABLE I

20.0 ml of $0.05N$ sodium vanadate solution + x ml of sulphuric acid solution + 10.0 ml of $0.05N$ sodium thiosulphate solution + water to make up the volume to 50.0 ml

Temperature 28°

Time of reaction (minutes)	Overall acid concentration				
	$0.04N$ H_2SO_4	$0.06N$ H_2SO_4	$0.2N$ H_2SO_4	$1.8N$ H_2SO_4	$2.7N$ H_2SO_4
5	incomplete	incomplete	incomplete	incomplete	incomplete
10	,,	,,	,,	,,	complete
20	,,	,,	,,	complete	,,
30	,,	,,	,,	,,	,,

From these results, it is seen that under conditions studied, the reaction is complete in 10 minutes at room temperature, only when the overall concentration of sulphuric acid is about $2.7N$ and higher. Further experiments have shown that the thiosulphate reacts completely in two to five minutes at the boiling water bath temperature, if the overall acid concentration is $0.06N$ and above. Many experiments were carried out at 98° at different sulphuric acid concentrations, varying the times of reaction. The results recorded in Table II show that the error of the determination increases with increasing concentration of sulphuric acid or with enhanced reaction time, keeping acid concentration constant. As the error is in every case positive, it is to be presumed that under such conditions, the further oxidation of tetrathionate to sulphate occurs

TABLE II

REACTION BETWEEN THIOSULPHATE AND EXCESS VANADIC ACID AT 98°

Amount of thiosulphate taken = 0.4471 millimols

Overall concentration of sulphuric acid	Time of reaction (minutes)	Millimols of thiosulphate reacting with vanadate as per equation for tetrathionate formation	Percentage difference
$0.06-0.08N$	5	0.4521	+1.12
$0.09-0.10N$	2	0.4521	+1.12
,,	5	0.4541	+1.57
,,	15	0.4563	+2.06
$0.12N$	5	0.4563	+2.06
,,	15	0.4584	+2.53
$0.15N$	5	0.4607	+3.04
$0.20N$	5	0.4649	+3.98

It is significant to note in this connection that LANG AND KURTENACKER[5] noticed that when the acid concentration is kept at $4N$, and the mixture boiled for 30 minutes, the thiosulphate is oxidized to sulphate quantitatively.

Catalysed reaction between vanadic acid and sodium thiosulphate

We have found that copper salts catalyse the oxidation of thiosulphate to tetrathionate by vanadic acid. The results of experiments carried out with copper sulphate as catalyst are recorded in Table III. It will be found that in the presence of the catalyst, the reaction goes to completion in the cold in 20 minutes, even when the concentration of sulphuric acid is as low as $0.05N$, whereas in absence of the catalyst the reaction will be complete in 20 minutes, only when the concentration of sulphuric acid is kept at $1.8N$ (Ref. Table I).

TABLE III

Cu^{+2} ION CATALYSED REACTION BETWEEN SODIUM THIOSULPHATE AND VANADIC ACID AT 28°

Amount of sodium thiosulphate taken = 0.4346

Overall concentration of sulphuric acid	Time of reaction (minutes)	Millimols of thiosulphate found by vanadate method	Percentage difference
0.05*N*	5	reaction incomplete	
,,	10	reaction incomplete	
,,	20	0.4408	+1.43
,,	30	0.4408	+1.43
0.06*N*—0.08*N*	5	incomplete	incomplete
,,	10	0.4408	+1.43
,,	20	0.4408	+1.43
0.10—0.12*N*	5	0.4408	+1.43
,,	10	0.4408	+1.43
,,	20	0.4408	+1.43
,,	30	0.4408	+1.43
0.16*N*	5	0.4408	+1.43
,,	30	0.4433	+2.00
0.20*N*	5	0.4433	+2.00
,,	30	0.4459	+2.60
0.30*N*	5	0.4454	+2.60
,,	30	0.4484	+3.18
0.40*N*	5	0.4509	+3.75

From the results in Table III, it will be seen that in the presence of Cu^{+2} ions, the reaction between sodium thiosulphate and vanadic acid is complete in 5 to 30 minutes at the room temperature, when the sulphuric acid concentration is varied between 0,1*N* to 0,05*N*, the error lying about 1.43%. If the acid concentration is increased beyond 0.16*N*, the error increases with increasing acid concentration and time of reaction and this appears to be due to the primary reaction product, namely tetrathionate, undergoing further oxidation to sulphate. Hence we propose that in order to limit the oxidation of sodium thiosulphate to the tetrathionate stage, with a view to using the reaction as the basis for a volumetric procedure, the sulphuric acid concentration should not be allowed to rise beyond 0.1*N*. The following procedure is recommended. An aliquot volume of the thiosulphate solution is run into a known excess of sodium vanadate solution (0.05*N*) containing 1.0 ml of 1% copper sulphate solution and enough sulphuric acid to keep the overall acidity at 0.1*N*. The mixture was in every case made up to 50 ml and kept for 5 minutes. The excess of unreacted vanadate was then titrated with standard ferrous ammonium sulfate solution, using diphenylbenzidine as indicator, after the addition of 5 ml of syrupy phosphoric acid and enough sulphuric acid to keep the acidity at 0.5 to 1.0*N*. Representative results are given in the Table IV.

TABLE IV

VANADAMETRIC ESTIMATION OF THIOSULPHATE THROUGH CONTROLLED OXIDATION TO TETRATHIONATE, IN SULPHURIC ACID MEDIUM WITH Cu^{+2} IONS AS CATALYST

Temperature of experiments 28° C

Millimols of thiosulphate taken	Millimols of thiosulphate found	Percentage error
0.8106	0.8153	0.62
0.7605	0.7643	0.52
0.6585	0.6624	0.61
0.5542	0.5606	1.10
0.4346	0.4408	1.36
0.2282	0.2344	2.60
0.2173	0.2217	1.80

Since acidity has been found to exert a critical influence on the course of the reaction between vanadic acid and sodium thiosulphate, it appeared to us that it would be advantageous to use a weak acid in place of a strong acid such as sulphuric acid; it might then be possible to avoid altogether the further oxidation of tetrathionate to sulphate. Hence experiments were carried in media acidified with trichloracetic acid, monochloracetic acid, formic acid and acetic acid instead of sulphuric acid. The results are recorded in Table V.

TABLE V

Cu^{+2} ION CATALYSED REACTION BETWEEN VANADIC ACID AND SODIUM THIOSULPHATE.
Temperature 28°
Amount of sodium thiosulphate taken: 0.2750 millimols
Total volume 50 ml; contains 1.0 ml of 1% copper acetate solution.

Acid used	Dissociation constant	Time of reaction	Amount of thiosulphate
5.0*N* H_2SO_4	strong acid	15 minutes	0.3005
		60 ,,	0.3175
5.0*N* CCl_3COOH	$20{,}000 \cdot 10^{-5}$	15 ,,	0.2825
		60 ,,	0.3005
5.0*N* $CH_2ClCOOH$	$155 \cdot 10^{-5}$	15 ,,	0.2750
		60 ,,	0.2750
		10 hours	0.2750
5.0*N* Formic acid	$21.4 \cdot 10^{-5}$	15 minutes	0.2750
		60 ,,	0.2750
		10 hours	0.2750
5.0*N* Acetic acid	$1.86 \cdot 10^{-5}$	15 minutes	0.2750
		1 hour	0.2750
		10 hours	0.2750

It will be seen from the above results that in media acidified with the strong acids, sulphuric (5*N*) and trichloracetic (5*N*) the reaction goes beyond the stage

References p. 514.

of tetrathionate; and this effect becomes greater as the time of reaction increases. With the weak acids acetic, formic, and monochloroacetic, the oxidation of thiosulphate proceeds only up to the tetrathionate stage in the experiments carried out at 28° and does not go up to the sulphate stage, even when kept for 10 hours. The copper ion catalysed reaction is completed even in 5 minutes. We observed a gradation in the times taken for completion of the uncatalysed reaction, in the case of the above three acids, which is of the same order as their dissociation constants. It has been observed that the oxidation was complete within 3 minutes with trichloroacetic acid, in 5 minutes with monochloroacetic acid and in 20 minutes with formic acid, whereas it is not complete even in 60 minutes with acetic acid. Since at room temperature the oxidation of tetrathionate to sulphate did not occur at all in media containing any of the three acids, monochloro, formic and acetic respectively, at 5.0*N* concentration, experiments have been made to ascertain if this would be the case at 98° as well. The results are given in Table VI.

TABLE VI

Cu^{+2} ION CATALYSED REACTION BETWEEN VANADIC ACID AND SODIUM THIOSULPHATE AT 98°

Amount of sodium thiosulphate taken = 0.2750 millimols

Acid used	Millimols of thiosulphate found	% Difference
5*N* monochloroacetic acid	0.3250	18.18
5*N* formic acid	0.2995	8.99
5*N* acetic acid	0.2750	nil

From these results, it is evident that in acetic acid medium, the oxidation of thiosulphate by vanadic acid, does not go beyond the tetrathionate stage even when heated to 98°. It is, therefore, safe to use acetic acid in place of a strong acid like sulphuric acid. When a strong acid is employed, it become necessary to control the concentration within certain critical limits, and also the time and temperature of the reaction; otherwise, the reaction proceeds to varying extents depending on the conditions. We have now found that, in the case of acetic acid, the concentration can be varied within wide limits (2-8*N*) and the time and temperature of reaction can also be varied within wide limits, without the risk of the tetrathionate undergoing further oxidation to sulphate.

In Table VII are given some typical results out of a large number of analyses carried out in acetic acid medium. The procedure adopted was as follows. An aliquot volume of the thiosulphate solution was run into a known excess of sodium vanadate solution (0.05*N*) containing acetic acid (2-8*N*) and copper acetate solution (1.0 ml of 1.0% solution) and the solution kept for 5 minutes. The volume of the reaction mixture was kept at 50 ml. Then the excess of unreacted vanadate was estimated by titration with standard ferrous ammonium sulphate solution using diphenylbenzidine as indicator, after adding 5 ml phosphoric acid and more acetic acid if necessary to keep the overall concentration at 5*N*.

TABLE VII

VANADAMETRIC ESTIMATION OF THIOSULPHATE THROUGH OXIDATION TO TETRATHIONATE IN ACETIC ACID MEDIUM WITH Cu^{+2} IONS AS CATALYST

Temperature of experiments 28°

Amount of thiosulphate taken in millimols	Amount of thiosulphate found in millimols	Percentage error
1.3750	1.3830	+0.58
1.1000	1.1070	+0.63
0.9625	0.9646	+0.22
0.7250	0.7265	+0.21
0.6875	0.6886	+0.16
0.5500	0.5511	+0.20
0.4125	0.4125	nil
0.2750	0.2750	nil
0.1375	0.1375	nil

The error of the determination thus varies from 0.16 to 0.63%.

Alternate vanadate method for the estimation of thiosulphate depending on its oxidation to tetrathionate

It is well known that ferric salts interact with thiosulphate as follows

$$2\ Fe^{+3} + 2\ S_2O_3^{-2} = 2Fe^{+2} + S_4O_6^{-2}$$

The reaction is rather slow and is known to be catalysed by copper salts. When thiosulphate is added to neutral ferric salt, a deep violet colour is produced owing to the formation of a complex ferric thiosulphate. On keeping, the colour gradually disappears and the solution contains tetrathionate and ferrous salt. LANG AND KURTENACKER[5] carried out the determination of thiosulphate by treating the same with an excess of ferric salt solution in the presence of copper salt, and then estimating the ferrous salt formed with ceric sulphate solution (but not with potassium permanganate). We have now modified this method using standard vanadate solution in place of Ce^{+4} solution to estimate the Fe^{+2} formed. The following procedure is recommended.

To an almost neutral solution of ferric alum (in excess) or ferric chloride, 5.0 ml of 1.0% copper sulphate solution are added followed by an aliquot (10-20 ml) of sodium thiosulphate solution and the mixture allowed to stand for about 5 to 10 minutes. The ferrous salt formed is then estimated by titration with standard sodium vanadate solution after the addition of the necessary quantities of sulphuric acid, phosphoric acid and diphenylbenzidine indicator solution. The vanadate consumed is a measure of the thiosulphate originally taken. The results recorded in Table VIII show that the method gives quite accurate results.

TABLE VIII

VANADAMETRIC ESTIMATION OF THIOSULPHATE THROUGH INTERACTION WITH FERRIC SALT

Millimols of sodium thiosulphate taken	Millimols of sodium thiosulphate found	Percentage error
0.1147	0.1147	—
0.1488	0.1497	0.6%
0.1584	0.1579	0.3%
0.1795	0.1785	0.56%
0.1926	0.1934	0.41%
0.2197	0.2197	—
0.2276	0.2284	0.35%
0.2548	0.2539	0.35%
0.2626	0.2634	0.31%
0.2809	0.2801	0.28%

SECTION II

Oxidation of thiosulphate to sulphate by vanadic acid

From the discussion in the preceding section, it is evident that sodium thiosulphate is oxidized by vanadic acid to sodium tetrathionate or sodium sulphate or both depending on the conditions. We have been able to lay down conditions under which the thiosulphate is oxidized only up to the tetrathionate stage quantitatively. In this section, we propose to discuss the conditions, under which the thiosulphate is entirely oxidized to the sulphate stage.

Our experiments described in Section I have shown that some oxidation to the sulphate stage occurs even in the cold, if the acidity of the medium is high; the higher the acidity the higher the percentage of thiosulphate oxidized to sulphate. LANG AND KURTENACKER[5] were able to achieve quantitative oxidation of thiosulphate to sulphate by treating it with excess of vanadic acid solution at 98° for 30 minutes at an overall concentration of $4.0N$.

We have now found that it is possible to oxidize the thiosulphate to sulphate quantitatively by vanadic acid even in the cold, if we carry out the reaction in the presence of $5N$ hydrochloric acid employing iodine monochloride as catalyst at a concentration of $0.005M$. For preparing the iodine monochloride solution, 0.279 g of potassium iodide and 0.178 g of potassium iodate were dissolved in

250 ml of water and made up to 500 ml with conc. HCl (d. 1.18). 1 ml of this solution was used as catalyst per 50 ml of reacting solution. The reaction can be quantitatively represented by the following equation.

$$Na_2 S_2O_3 + 4(O) + H_2O = Na_2SO_4 + H_2SO_4$$

For carrying out an estimation, the following conditions were adopted. To an excess of standard sodium vanadate solution (20 ml of 0.25*N* or 0.05*N*) taken in a conical flask was added 1.0 ml of the iodine monochloride and 10 ml of sodium thiosulphate solution. Then, 30 ml of 10*N* HCl was added to the mixture during the course of a minute with shaking. The mixture was kept for 10 minutes and the excess vanadate estimated by titration with standard ferrous ammonium sulphate solution with diphenylbenzidine as indicator, diluting if necessary. While estimating larger amounts of the thiosulphate, 0.25*N* vanadate was employed, and 0.05*N* vanadate was used for lower amounts of the thiosulphate. In the latter case, N-phenylanthranilic acid can also be used as the indicator with greater satisfaction. Some typical results are given in Table IX.

TABLE IX

OXIDATION OF THIOSULPHATE TO SULPHATE AT 28° BY VANADIC ACID USING IODINE MONOCHLORIDE AS CATALYST

Amount of thiosulphate taken	Amount of thiosulphate oxidized to sulphate	Percentage error
0.0250	0.0250	nil
0.0350	0.0350	nil
0.0525	0.0525	nil
0.0700	0.0701	0.14
0.0875	0.0875	nil
0.1120	0.1121	0.08
0.2240	0.2241	0.04
0.3920	0.3922	0.05
0.5600	0.5611	0.20
0.6720	0.6745	0.35
0.8400	0.8424	0.30
1.1200	1.1256	0.50
1.4600	1.4720	0.80

As this part of the investigation was completed, our attention has been drawn to the publication of BALWANT SINGH AND RANJIT SINGH[10] giving an account of the estimation of sodium thiosulphate, by titration with a solution of sodium metavanadate using iodine monochloride as a preoxidizer and catalyser, and chloroform as indicator. The conditions employed by these workers are very different from those employed by us, as also the mode of titration. A known amount of the substance was taken in a conical flask and about 25 ml of water, 30 ml of conc. HCl, 5 ml of 0.02*M* iodine monochloride and 5 ml of chloroform were added to it. The mixture was cooled to room temperature and titrated against standard sodium metavanadate solution. The reagent was added from a

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burette until the solution which was coloured with iodine became pale green and the chloroform layer acquired a purple colour due to iodine. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of metavanadate solution was continued, shaking vigorously after each addition, until the chloroform layer was faintly violet. The metavanadate was then added dropwise, with shaking after the addition of each drop until the chloroform layer became light pale yellow. The end-point was claimed to be very sharp. In these titrations, the normality of the solution with respect to hydrochloric acid was kept between $7N$ to $7.5N$ even at the end-point by the addition of more acid.

The concentration of hydrochloric acid and of iodine monochloride was lower in our experiments than in those of BALWANT SINGH AND RANJIT SINGH; the detection of end-point in their method requires considerable practice and experience; and the amounts of thiosulphate that can be estimated cannot be high on account of the risk of precipitation of sulphur because of the reaction of thiosulphate with the acid. The vanadametric method which we developed is not subject to these disadvantages.

SUMMARY

1. (a) We have found that sodium thiosulphate is quantitatively oxidized to tetrathionate in five minutes at room temperature (28°) by excess sodium vanadate in a medium containing sulphuric acid at $0.06N$ to $0.1N$ concentration and a little copper sulphate as catalyst.

(b) Quantitative oxidation of sodium thiosulphate to tetrathionate has also been achieved by the action of excess sodium vanadate during five minutes at room temperature in a medium containing $2.0N$—$8.0N$ acetic acid and a little copper salt as catalyst. Further oxidation to sulphate does not occur, even if the mixture is heated to boiling.

(c) The excess of unreacted vanadate in 1 (a) and 1 (b) can be titrated with a standard solution of ferrous ammonium sulphate using diphenylbenzidine as indicator, after adding the requisite quantity of syrupy phosphoric acid.

2. On the other hand, sodium thiosulphate is easily and quantitatively oxidized to sulphate at room temperature, when acted upon by excess sodium vanadate in a medium containing hydrochloric acid at an overall concentration of 5-$6N$ and 1.0 ml of iodine monochloride as catalyst. The time required for reaction is ten minutes. The unreacted vanadate can be estimated by titration with a standard solution of ferrous ammonium sulphate, using N-phenylanthranilic acid as indicator or with diphenylbenzidine as indicator after suitably diluting and adding phosphoric acid.

RÉSUMÉ

1. (a) Les auteurs ont constaté que le thiosulfate de sodium est oxydé quantitativement en tétrathionate, en 5 minutes, à la température ambiante (28°), par un excès de vanadate de sodium, en milieu sulfurique $0.06N$-$0.1N$, en présence de sulfate de cuivre comme catalyseur.

(b) L'oxydation quantitative du thiosulfate de sodium en tétrathionate peut également s'effectuer en solution acétique $2.0N$-$8.0N$, par un excès de vanadate de sodium, en 5 minutes, à la température ambiante, en présence d'un sel de cuivre,

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comme catalyseur. Des oxydations ultérieures en sulfate ne se produisent pas, même si le mélange est porté à ébullition.

(c) L'excès de vanadate (de 1(a) et de 1(b)) peut être titré par une solution étalon de sel de Mohr en présence de diphénylbenzidine comme indicateur, après addition d'acide phosphorique concentré.

2. D'autre part, le thiosulfate de sodium peut être facilement et quantitativement oxydé en sulfate, à la température ordinaire, par un excès de vanadate de sodium en solution chlorhydrique 5-6*N* et en présence de 1 ml de monochlorure d'iode comme catalyseur. Cette réaction dure 10 minutes. L'excès de vanadate peut être titré par une solution de sel de Mohr, en présence d'acide N-phénylanthranilique ou de diphénylbenzidine comme indicateur, après dilution et addition d'acide phosphorique.

ZUSAMMENFASSUNG

1. (a) Die Autoren haben festgestellt, dass das Natriumthiosulfat in 5 Minuten bei einer Temperatur von 28° quantitativ zu Tetrathionat oxydiert wird, durch einen Überschuss an Natriumvanadat in einer schwefelsauren Lösung 0.06-0.1*N* in Gegenwart von Kupfersulfat als Katalisator.

(b) Die quantitative Oxydation von Natriumthiosulfat zu Tetrathionat kann auch in 5 Minuten bei der genannten Temperatur in einer essigsauren Lösung 2.0-8.0*N* durch einen Überschuss von Natriumvanadat in Gegenwart eines Kupfersalzes, als Katalisator durchgeführt werden. Weitere Oxydationen zu Sulfat finden nicht statt, selbst wenn man die Mischung zum sieden bringt.

(c) Der Überschuss von Vanadat (von 1(a) und 1(b)) kann mit einer Vergleichslösung von Mohrschem Salz titriert werden, in Gegenwart von Diphenylbenzidin als Indikator, nachdem konzentrierte Phosphorsäure zugegeben wurde.

2. Anderseits kann das Natriumthiosulfat leicht und quantitativ bei gewöhnlicher Temperatur zu Sulfat oxydiert werden, durch einen Überschuss von Natriumvanadat in Salzsäure 5-6*N* und in Gegenwart von 1 ml Jodmonochlorid als Katalisator. Diese Reaktion dauert 10 Minuten. Nach der Verdünnung und der Zugabe von Essigsäure kann der Überschuss an Vanadat durch eine Mohrsche-Salzlösung titriert werden, in Gegenwart von N-phenyl-anthranil-Säure oder Diphenylbenzidin als Indikator.

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CHEMISTRY OF THORIUM
II. VOLUMETRIC DETERMINATION OF THORIUM

by

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Various reagents have been proposed for the gravimetric determination of thorium in neutral as well as acid media. Mention may be made of the *m*-nitrobenzoic acid method of NEISH[1] in neutral medium, the iodate method of MEYER AND SPATER[2] in 40% of nitric acid, and the pyrophosphate method of CARNEY AND CAMPBELL[3] in acid medium. Various organic acids of different types have been tried for the gravimetric determination of thorium by RAGHAVA RAO and his co-workers[4]. A radioactive procedure of estimation of thorium in monazite has been developed by MOELLER AND SCHWEITZER[5] following the method of CARNEY AND CAMPBELL[3], using a measured excess of standard sodium pyrophosphate solution containing a known quantity of radio-active phosphorus (^{32}P) and determining the excess by measurement of its radioactivity.

Very few volumetric procedures for the estimation of thorium are known. The iodate method of MEYER AND SPATER[2] has been utilized by MOELLER AND FRITZ[6] for the titrimetric determination of thorium through the iodometric estimation of the iodate content of the precipitate by dissolving in sulphuric acid and adding potassium iodide. This makes the method more rapid. The rapid thermometric titration method has been tried with success by one of us (N. K. DUTT[7]) for the determination of thorium in presence of phosphoric acid and rare earths in 1*N* HCl medium with sodium pyrophosphate.

For sake of rapidity and quickness, a search for other volumetric methods was found necessary. NEISH (*loc. cit.*) in his original *m*-nitrobenzoic acid method advised the ignition of the moist precipitate and weighing as ThO_2. That consumes much time. The present authors have shown that the thorium *m*-nitrobenzoate can be weighed directly in a Gooch crucible after final washing with alcohol and drying at 105° C. To prevent hydrolysis NEISH advised washing of the precipitate with 5% solution of the precipitant (saturated solution of *m*-nitrobenzoic acid). He found that there was no necessity to remove the adhering wash liquid for gravimetric purpose. This was, however, found necessary in the present case and was easily accomplished by washing with alcohol in which the reagent is highly soluble whereas the thorium compound is insoluble, as NEISH observed.

Volumetric adaptation of the above method

There is one familiar volumetric method for the determination of organic nitro-compounds by treatment with excess standard titanous chloride and titrating the excess of the reagent with standard ferric alum. The method is the result of the comprehensive researches of KNECHT AND HIBBERT[8] and was later modified by ENGLISH[9] and used for the determination of various organic nitro-compounds. It has been shown by the present authors that *m*-nitrobenzoic acid can similarly be estimated very accurately by titanous chloride. This fact at once suggests that a volumetric method may be developed if the *m*-nitrobenzoic acid content of the precipitated thorium salt is determined volumetrically. This has actually been accomplished with success and thorium has been determined volumetrically. The success of the method depends upon the fact that the thorium compound has a definite composition and can be weighed directly in a Gooch crucible after removing the adhering wash liquid with alcohol. This has been verified previously as shown.

EXPERIMENTAL

Thorium solution — the sample of thorium nitrate used was supplied by E. Merck and Co. Thorium nitrate solution was standardized by precipitation with oxalic acid and subsequent ignition to dioxide.

m-Nitrobenzoic acid — this reagent was also supplied by E. Merck and Co. The sample was recrystallized several times from alcohol and dried in an air oven at 110° C, m.p. 141° C.

Determination of thorium by direct weighing in a Gooch crucible

The procedure has been the very same as that described by NEISH. The precipitate is filtered in a Gooch, washed at first with a 5% solution of the precipitant and finally with alcohol till free from acid. The crucible is then dried in an air oven at 105° C till constant weight. Good results have been obtained. Thorium is weighed as $Th(C_7H_4NO_4)_4$ (ThO_2-29.46%). The results are shown in Table I.

TABLE I

Wt of Th compound g	ThO_2 found g	ThO_2 taken g	Error g
0.0652	0.0192	0.0194	— 0.0002
0.0985	0.0290	0.0292	— 0.0002
0.1616	0.0476	0.0480	— 0.0004
0.2287	0.0672	0.0672	0
0.1618	0.0478	0.0480	— 0.0002
0.1625	0.0480	0.0480	0
0.0814	0.0240	0.0242	— 0.0002
0.0817	0.0242	0.0242	0

Determination of m*-nitrobenzoic acid*

Experimental arrangements and analytical procedures were the same as those described by English for the determination of other aromatic nitro-compounds. All precautionary measures advised were strictly adhered to. Results are shown in Table II.

TABLE II

m-nitrobenzoic acid

Taken g	Found g
0.0191	0.0192
0.0188	0.0186
0.0183	0.0183
0.0187	0.0188

Volumetric determination of thorium

For the volumetric determination of thorium, thorium nitrobenzoate was precipitated according to the method of Neish. The precipitate was finally washed with alcohol till free from acid. As some difficulty was encountered in transferring the precipitate from the filter, it was taken along with the paper in the reaction flask and treated with 25 ml of 40% sulphuric acid and 25 ml of water. The rest of the procedure was the same as that for pure *m*-nitrobenzoic acid. While standardizing the titanous chloride with ferric alum by a similar process, one quantitative filter paper moistened with alcohol was always taken in the reaction vessel. Results are shown in Table III.

Further work with this reagent and other organic nitro-derivatives are in progress.

TABLE III

ThO_2 found g	ThO_2 taken g	Error g
0.0121	0.0121	0
0.0121	0.0121	0
0.0121	0.0121	0
0.00967	0.00962	+ 0.00005
0.0121	0.0121	0
0.01442	0.0144	+ 0.00002
0.0096	0.00962	— 0.00002
0.01442	0.0144	+ 0.00002

SUMMARY

Thorium has been determined volumetrically. It has been precipitated with *m*-nitrobenzoic acid according to the method of NEISH. Thorium *m*-nitrobenzoate has been then dissolved in sulphuric acid and titrated with titanous chloride to determine the NO_2-group which gives the amount of thorium directly.

RÉSUMÉ

Une méthode volumétrique est proposée pour le dosage du thorium. Celui-ci est précipité par l'acide *m*-nitrobenzoïque selon la méthode de NEISH. Le *m*-nitrobenzoate de thorium est ensuite dissous dans l'acide sulfurique. On titre les groupements NO_2 au moyen de chlorure de titane(III), ce qui donne directement la teneur en thorium.

ZUSAMMENFASSUNG

Es wird eine volumetrische Methode vorgeschlagen, für die Bestimmung von Thorium. Dieses wird ausgefällt mit *m*-Nitrobenzolsäure nach der Methode NEISH. Das Thorium-*m*-nitrobenzoat wird darauf in Schwefelsäure gelöst. Man titriert die NO_2-Gruppen mit Titan(III) chlorid, welches direkt den Gehalt an Thorium gibt.

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ESTIMATION OF METALS AS SULPHIDES
III. ESTIMATION OF RHENIUM, SILVER AND MERCURY

by

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In a number of publications[1,2,3,4] from this laboratory it was shown that certain elements can be conveniently precipitated and estimated as sulphides by decomposing their thiosalts and weighing the precipitated sulphides after suitable treatment. It was also shown that some metals which do not form thiosalts can be precipitated and estimated as sulphides more conveniently by precipitating the sulphide by means of an alkali sulphide under suitable conditions. It has been found that the method can also be extended to rhenium, silver and mercury.

EXPERIMENTAL

Estimation of rhenium as sulphide

The most reliable method for the estimation of rhenium consists in precipitating it as hepta-sulphide by passing hydrogen sulphide for 2-3 hours into a solution containing 30-35% hydrochloric acid by volume and heating to a temperature of 90°-95° C. The sulphide is converted to perrhenate by means of 5% sodium hydroxide and 30% hydrogen peroxide, the solution is treated with nitron acetate and the precipitate is dried and weighed.

It is well-known that rhenium forms a thiosalt on treatment with alkali sulphide and the thiosalt decomposes on adding excess of acid with the precipitation of the hepta-sulphide. But, as has been seen in the case of other elements dealt with already, the complete decomposition of the thiosalt and the formation of a precipitate which is suitable for gravimetric estimation depends upon the conditions under which the thiosalt is decomposed. Thus in the case of rhenium, treatment with excess of acetic acid and ammonium acetate which was so successful in the case of platinum metals[5] fails to decompose the thiosalt completely and gives low results. Treatment with dilute hydrochloric acid also fails to precipitate the sulphide completely. It is only when the thiosalt is treated with a large excess of concentrated hydrochloric acid that the thiosalt is decomposed, but the precipitate of sulphide obtained in this case has a great tendency to stick to the sides of the beaker. After trying the action of a number of reagents it was ultimately found that if the thiosalt is decomposed with concentrated hydrochloric acid in the presence of a large amount of ammonium sulphate, the thiosalt is not only decomposed completely but the sulphide is obtained in an easily filterable form. The precipitate of the sulphide after suitable treatment can be weighed directly. It does not lose weight on heating upto 160° C.

For estimating rhenium as sulphide a solution of potassium perrhenate was prepared and standardized[6] by the sulphide-nitron method referred to above. Measured portions of this solution were treated with excess of the alkali sulphide reagent, followed by a large excess of concentrated hydrochloric acid and ammonium sulphate (20-25 grams), the resulting normality of the hydrochloric acid in the mixture being about 6*N*. On heating the turbid mixture to boiling the sulphide was completely precipitated and the precipitate settled satisfactorily when cooled to room temperature (cooling in ice-cold water hastens the settling). The precipitate was filtered through a sintered glass crucible (porosity 4) under very low pressure, washed free from chloride ions with water, and then with alcohol and ether successively, sucked dry at the filter pump, dried in a vacuum desiccator for half an hour and weighed as Re_2S_7.

The weights of metallic rhenium contained in a measured portion of the solution and those corresponding with the precipitate actually obtained are given in Tables I and II.

Estimation of silver

Although silver sulphide is insoluble in dilute acid and alkaline solutions, silver is not usually estimated as sulphide. This is probably because the precipitate becomes contaminated with free sulphur which forms as a result of the oxidation of the alkali sulphide.

A careful study of the conditions under which silver can be precipitated as sulphide has, however, shown that the metal can be estimated as sulphide by adding a slight excess of alkali sulphide to an ammoniacal solution of silver. The precipitate has only to be washed with water, alcohol and ether successively, dried in a vacuum desiccator and weighed. If the alkali sulphide reagent is prepared at a low temperature and added to an ammoniacal solution containing silver the precipitate of silver sulphide was found to be free from sulphur.

For estimating silver as sulphide a solution of silver nitrate (AnalaR quality) was prepared and standardized[7,8] by precipitation as silver chloride or by VOLHARD's method. Measured portions of the silver solution were treated with ammonium hydroxide until a clear solution was obtained. The ammoniacal solution was then treated with an excess of the alkali sulphide reagent and the mixture was shaken until the precipitate coagulated completely. The precipitate was filtered through a sintered glass crucible (porosity 4) washed thoroughly with cold water, alcohol and ether successively, sucked dry at the filter pump, dried in a vacuum desiccator for half an hour and weighed as Ag_2S.

TABLE I

DETERMINATION OF RHENIUM WITH 2*N* SODIUM SULPHIDE REAGENT

Vol of Re solution in ml	Vol of reagent added in ml	Vol of 12*N* hydrochloric acid added in ml	Wt of ppt Re_2S_7 in g	Wt of Re in the ppt in g	Wt of Re actually present in g
5	50	60	0.0247	0.01543	0.01539
10	45	55	0.0493	0.03079	0.03077
25	50	55	0.1232	0.07695	0.07695
10	60	70	0.0347	0.02167	0.02164
10	70	80	0.0346	0.02161	0.02164
25	60	70	0.0866	0.05409	0.05409
25	65	90	0.0559	0.03491	0.03497
25.14	65	90	0.0562	0.03510	0.03518
25.26	65	90	0.0565	0.03529	0.03534

TABLE II

DETERMINATION OF RHENIUM WITH 1*N* AMMONIUM SULPHIDE REAGENT

Vol of Re solution in ml	Vol of reagent added in ml	Vol of 12*N* hydrochloric acid added in ml	Wt of ppt Re_2S_7 in g	Wt of Re in the ppt in g	Wt of Re actually present in g
5	50	60	0.0247	0.01543	0.01539
10	55	60	0.0493	0.03079	0.03077
25	55	60	0.1232	0.07695	0.07695
10	60	70	0.0346	0.02161	0.02164
25	60	75	0.0865	0.05403	0.05409
25.60	65	90	0.0886	0.05534	0.05540
25.60	65	85	0.0887	0.05540	0.05540
20	60	70	0.0447	0.02792	0.02799
25	75	90	0.0559	0.03491	0.03497

The weights of the metallic silver contained in the measured portions of the solution and those corresponding with the precipitate actually obtained are given in Tables III and IV.

TABLE III

DETERMINATION OF SILVER WITH 2*N* SODIUM SULPHIDE REAGENT

Vol of Ag solution in ml	Vol of reagent added in ml	Wt of ppt Ag_2S in g	Wt of Ag in the ppt in g	Wt of Ag actually present in g
10	10	0.1212	0.1055	0.10550
20	10	0.1036	0.0902	0.09016
25	10	0.2819	0.2455	0.24550
25.60	40	0.0940	0.08185	0.08185
25.60	30	0.0972	0.08465	0.08470
25.94	40	0.0950	0.08271	0.08275
25.18	25	0.0924	0.08046	0.08069
25	40	0.0920	0.08011	0.08011
26.22	50	0.2852	0.2483	0.2484

TABLE IV

DETERMINATION OF SILVER WITH 1*N* AMMONIUM SULPHIDE REAGENT

Vol of Ag solution in ml	Vol of reagent added in ml	Wt of ppt Ag_2S in g	Wt of Ag in the ppt in g	Wt of Ag actually present in g
10	10	0.1127	0.09811	0.09817
10	20	0.1128	0.09819	0.09817
25	20	0.2818	0.2453	0.24550
26.20	50	0.0962	0.08377	0.08377
51.24	40	0.1870	0.1629	0.16320
25.10	30	0.0918	0.07993	0.08009
25.08	35	0.0858	0.07471	0.07480
25.18	30	0.2734	0.2381	0.23850
25.60	40	0.2786	0.2425	0.24260

Estimation of mercury

The estimation of mercury by VOLHARD's method[9,10] is well established and gives accurate results. But experiments carried out in this laboratory on the precipitation of mercuric sulphide have shown that equally good results are obtained by treating a mercuric salt with excess of alkali sulphide and then acidifying the solution with hydrochloric acid. If the alkali sulphide solution is prepared by passing hydrogen sulphide into the alkali solution at a low temperature the precipitate of mercuric sulphide is practically free from sulphur and can be weighed after washing with alcohol and ether successively and heating to 105° C. The contamination of the precipitated mercuric sulphide with free sulphur in VOLHARD's method is due probably to the oxidation of the alkali sulphide on heating.

For estimating mercury as sulphide a solution of mercuric chloride (AnalaR quality) was prepared and standardized according to VOLHARD's method. Measured portions of this solution were treated with ammonium hydroxide until a slight turbidity appeared and then with an excess of freshly prepared alkali sulphide reagent (prepared by passing hydrogen sulphide below 5° C). The precipitate of sulphide which is formed does not dissolve if ammonium sulphide is used, while it dissolves partially or completely in the sodium sulphide reagent. The mixture was acidified with hydrochloric acid, heated to boiling, allowed to settle and filtered through a sintered glass crucible (porosity 4). The precipitate of mercuric sulphide was washed with water until it was free from chloride ions and then with alcohol and ether successively. It was then heated to 105° C for about an hour and weighed as HgS.

The weights of metallic mercury contained in measured portions of the solution and those corresponding with the precipitate actually obtained are given in Tables V and VI.

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TABLE V

DETERMINATION OF MERCURY WITH $2N$ SODIUM SULPHIDE REAGENT

Vol of Hg solution in ml	Vol of reagent added in ml	Vol of $2N$ hydrochloric acid added in ml	Wt of ppt HgS in g	Wt of Hg in the ppt in g	Wt of Hg actually present in g
8	20	30	0.1034	0.08915	0.08915
20	45	55	0.2584	0.2228	0.22290
20	50	60	0.2584	0.2228	0.22290
20	25	30	0.0986	0.08502	0.08502
20	30	35	0.0985	0.08493	0.08502
20	35	40	0.0985	0.08493	0.08502
26.97	25	35	0.1171	0.1010	0.10130
27.92	30	40	0.1214	0.1047	0.10470
25.84	50	60	0.1123	0.09685	0.09699

TABLE VI

DETERMINATION OF MERCURY WITH $1N$ AMMONIUM SULPHIDE REAGENT

Vol of Hg solution in ml	Vol of reagent added in ml	Vol of $2N$ hydrochloric acid added in ml	Wt of ppt HgS in g	Wt of Hg in the ppt in g	Wt of Hg actually present in g
8	15	20	0.1034	0.08915	0.08915
20	25	30	0.2585	0.2229	0.22290
20	30	35	0.2584	0.2228	0.22290
20	30	20	0.0985	0.08493	0.08502
20	35	25	0.0986	0.08502	0.08502
26.80	30	40	0.1166	0.1006	0.10060
19.30	25	35	0.0840	0.07244	0.07268
26.12	45	55	0.1136	0.09797	0.09802
25	55	65	0.1088	0.09383	0.09383

Note on the behaviour of germanium

Germanium forms a thiosalt with alkali sulphides. On treatment with excess of concentrated hydrochloric acid the thiosalt is decomposed with the precipitation of the white GeS_2. It was, therefore, expected that it would be possible to estimate germanium by decomposing the thiosalt and weighing the precipitated sulphide as in the case of other metals. But actual experiments made with this object in view proved unsuccessful. Germanium sulphide is precipitated completely, but it has a great tendency to become peptized with the result that when the precipitate is washed with water or alcohol it passes into the filtrate. On washing with $6N$ hydrochloric acid there is practically no peptization but if the precipitate containing some hydrochloric acid is heated in an air oven rapid loss in weight of the precipitate occurs owing probably to the decomposition of sulphide with the the formation of volatile germanium tetra-chloride. Peptization of the precipitate can also be prevented by washing with concentrated ammonium chloride but this also leads to the decomposition of the sulphide as in the case of hydrochloric acid. Attempts were also made to convert the precipitate of germanium sulphide (which had been washed with 6*N* hydrochloric acid) into germanium oxide by treatment with ammonium hydroxide and hydrogen peroxide but results obtained were not satisfactory.

SUMMARY

1. It has been shown that under proper conditions rhenium, mercury and silver can be precipitated quantitatively as pure sulphides and the precipitate weighed directly for the estimation of the metal.

2. In the case of rhenium the solution containing perrhenate is treated with excess of alkali sulphide and the resulting solution containing the thiosalt is treated with excess of concentrated hydrochloric acid and ammonium sulphate. The precipitate is weighed directly as Re_2S_7.

3. In the case of silver the metal in ammoniacal solution is treated with excess of alkali sulphide and the precipitate weighed directly as Ag_2S.

4. In the case of mercury, the solution containing the metal is treated with excess of alkali sulphide solution in the cold followed by excess of hydrochloric acid. The precipitate obtained under these conditions is completely free from sulphur and can be weighed directly as HgS.

5. Although germanium forms a thiosalt which decomposes with excess of hydrochloric acid, it was found that the metal cannot be estimated as sulphide owing to the peptization of the precipitate on washing and its decomposition on heating.

RÉSUMÉ

1. Il a été démontré que, dans certaines conditions, le rhénium, le mercure et l'argent peuvent être précipités quantitativement comme sulfures purs et que le précipité peut être pesé directement pour le dosage de ces métaux.

2. Dans le cas du rhénium, la solution renfermant le perrhénate est traitée par un excès de sulfure alcalin et la liqueur obtenue renfermant le thiosel par un excès d'acide chlorhydrique concentré et de sulfate d'ammonium. Le précipité est pesé directement comme Re_2S_7.

3. Dans le cas de l'argent, sa solution ammoniacale est traitée par un excès de sulfure alcalin et le précipité est pesé directement comme Ag_2S.

4. Dans le cas du mercure, sa solution est traitée à froid par une solution de sulfure alcalin en excès puis par un excès d'acide chlorhydrique. Le précipité obtenu dans ces conditions est tout à fait exempt de soufre et il peut être pesé directement comme HgS.

5. Bien que le germanium forme un thiosel décomposable par l'acide chlorhydrique en excès, il ne peut être dosé ainsi sous forme de sulfure, il y a peptisation lors du lavage et décomposition lors du chauffage.

ZUSAMMENFASSUNG

1. Es wird gezeigt, dass unter bestimmten Bedingungen Rhenium, Quecksilber und Silber quantitativ als reine Sulfide gefällt werden können, und dass der Niederschlag für die Bestimmung dieser Metalle direkt gewogen werden kann.

2. Im Falle des Rheniums wird die Lösung, welche Perrhenat enthält, mit einem Überschuss von Alkalisulfid behandelt, und die erhaltene Flüssigkeit, welche das Thiosalz enthält, mit einem Überschuss von konzentrierter Salzsäure und mit Ammoniumsulfat behandelt. Der Niederschlag wird direkt als Re_2S_7 gewogen.

3. Im Falle des Silbers wird die ammoniakalische Lösung mit einem Überschuss von Alkalisulfid behandelt, und der Niederschlag wird direkt als Ag_2S gewogen.

4. Im Falle des Quecksilbers wird die Lösung zuerst mit einer Lösung von Alkalisulfid im Überschuss behandelt, und nachher mit einem Überschuss von Salzsäure. Unter diesen Bedingungen ist der erhaltene Niederschlag vollständig frei von Schwefel und kann direkt als HgS gewogen werden.

5. Obwohl das Germanium ein durch einen Salzsäureüberschuss zersetzbares Thiosalz bildet, kann es nicht in Form eines Sulfides dosiert werden, da es beim Waschen peptisiert und beim Erhitzen sich zersetzt.

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DETERMINATION OF OXYGEN IN CERTAIN GASES

IMPROVED WINKLER METHOD

by

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The present day techniques for preparing oxygen-free materials and for studying the effects of corrosion of metals by liquids demand gaseous blankets free of, or nearly free of oxygen. For these reasons methods for the determination of oxygen in gases (1 to 10 parts per million) have been studied extensively.

Instruments for the determination of oxygen such as the Beckman Oxygen Analyser based on the theory of PAULING's[1] Oxygen Meter or the mass spectrometer are not readily adaptable to the detection of such small quantities.

Many colorimetric methods have been developed, but with the exception of that of BRADY[2], none are sensitive enough to determine one part per million oxygen. However, BRADY's method requires an oxygen free-carrier gas, (which is a difficult problem in itself) as well as large volumes of gas to obtain sufficient oxygen for measurement.

The WINKLER[3] method, in which oxygen is absorbed into a neutral or alkaline manganous solution and then determined by titration or by color, is one of the older methods for oxygen. Instead of the iodide color, HASLAM AND MOSES[4] thought the color change effected with *ortho*-toluidine would be more satisfactory, and later SZABO[5] suggested an oxalic acid titration, but neither of these methods was adaptable to the determination of micro-quantities of oxygen.

The original iodine method was frequently modified, for lower oxygen determinations. MEYER AND GHIJSEN[6] and TAYLOR AND ALEXANDER[7] used such a method for oxygen concentrations up to 4.0% oxygen. Neither method, however, had blanks low enough to justify use in the parts per million range.

VAN STRATEN[8] modified these methods so as to obtain a moderately low blank, and to provide for maximum oxygen absorption by the manganous solution. This method was reliable and accurate over the range of 0.1 (1000 parts per million) to 4.0% oxygen by volume. The minimum amount detectable, (actually the blank) was 10 parts per million oxygen with a standard deviation of 13 parts per million in this range.

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WINSLOW AND LIEBHAFSKY[9] could determine oxygen in the parts per million range but their method required large quantities of sample. PEPKOWITZ AND SHIRLEY[10] reduced the amount of sample necessary by suggesting the determination of iodine by a colorimetric method. Investigation of this latter method proved its sensitivity to small quantities of oxygen but showed that more care would be necessary to make the reagents oxygen-free. A blank greater than one part per million was obtained when the PEPKOWITZ method was used; further study showed an important error in technique and that the method must be changed from a pressure-type system to a vacuum-type system.

If the WINKLER method is to be used for small amounts of oxygen several conditions must be met:

1. A solution of manganous ion free from manganic ion must be available.

2. Oxygen dissolved in the liquid reagents used in the analyses must be removed.

3. Atmospheric oxygen *must* be excluded from the sample until after the iodine has been extracted from the aqueous solution.

4. A sensitive and accurate method of determining the released iodine must be used.

Manganous solution. Both PEPKOWITZ AND SHIRLEY[10] and VAN STRATEN[8] recognized the difficulty of preparing a reagent free of manganic ion. PEPKOWITZ AND SHIRLEY incompletely dissolved manganese metal in dilute sulfuric acid, hoping that the excess metal would reduce any manganic ion. However, erratic results were noted when this plan was used; further the manganese concentration varied from batch to batch. According to VAN STRATEN and TAYLOR AND ALEXANDER, such variations in concentration of manganese have important effects on oxygen absorption.

VAN STRATEN de-aerated the manganese solution, but this does not reduce manganic ion which is expected to be present. Best results are obtained when a slightly acidic solution of manganous chloride is heated to boiling while purging with carbon dioxide (Table I).

Removal of oxygen from the alkali and potassium iodide reagents. The pre-treatment of these reagents was studied (Table II) and showed that the alkali is best made up quickly in boiled water and de-aerated with helium while the potassium iodide reagent is being made up separately in water and de-aerated with carbon dioxide; the two are mixed just prior to use. It is not advisable to de-aerate the alkali with carbon dioxide, since the absorbed carbonate precipitates some unusable manganous carbonate.

Exclusion of atmospheric oxygen from the sample. PEPKOWITZ AND SHIRLEY extracted iodine into toluene from an aqueous iodide-manganous chloride solution in the presence of air, but our tests showed that this aqueous solution

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TABLE I

EFFECT OF VARIOUS TREATMENTS OF MANGANOUS CHLORIDE SOLUTION FOR REAGENT BLANKS

(Using untreated potassium iodide reagent)

Treatment	Optical density in 10 ml *o*-xylene	Equivalent μl O_2/l	Average ppm (blank)
1. Pepkowitz method	0.185 ± 0.075*	24.9 ± 10.1	24.9 ± 10.1
2. Manganous chloride solution, boiled and purged, but not freshly prepared	0.072	9.7	9.7
3. Treatment of manganous solution just before using			
a. Purging with CO_2 in cold	0.070	9.5	5.7 ± 4.0
	0.013	1.8	
b. Purging with CO_2 while heating to boiling	0.017	2.3	5.27 ± 1.9
	0.042	5.7	
	0.029	4.0	
	0.049	6.6	
c. Purging with CO_2 while hot, for 10 min	0.087	11.7	7.5 ± 4.2
	0.024	3.3	

* An average of numerous determinations

TABLE II

EFFECT OF VARIOUS TREATMENTS OF KI-NaOH SOLUTIONS FOR REAGENT BLANKS

Treatment	Optical density in 10 ml *o*-xylene	Equivalent μl O_2/l	Average ppm (blank)
1. Boiled water, added KI and NaOH	0.0625	8.4	8.4
2. Boiled combined KI-NaOH solution	0.053	7.2	—
3. Made up separately, boiled, then mixed	0.038	5.1	—
4. Boil combined KI-NaOH solution, while purging with CO_2	0.018	2.4	3.5 ± 1.1
	0.033	4.7	
5. Make up separately, boil, add reagent, cool while purging, and mix just before using	0.008	1.0	1.15 ± 0.17
	0.010	1.3	
	0.010	1.3	
	0.008	1.0	
6. Make up NaOH with He purging, add KI crystals just before using	0.038	5.2	4.6 ± 0.6
	0.030	4.1	
	0.033	4.5	
7. Make up NaOH with He purging, KI with CO_2 purging	0.020	2.3	2.5 ± 0.2
	0.017	2.3	
	0.020	2.8	
	0.018	2.5	
	0.019	2.6	

(WINKLER) is sufficiently sensitive to oxidation by air to vitiate results. Extractions equivalent to 50 parts per million or more of oxygen (depending on the time of extraction) were obtained in this manner.

In the proposed procedure, the organic extracting agent is added under vacuum and the iodine is extracted under vacuum. Vacuum stopcocks are used throughout.

A sensitive and accurate extractant for iodine. Ortho-xylene was found to be superior to toluene, *para-* or *meta*-xylene, *para*-cymene, cumene and other organic reagents as extractant for iodine. It is superior to toluene in terms of sensitivity to small changes in iodine concentration, in stability of color, and in production of a low blank.

EXPERIMENTAL

A. *Solvent studies*

Many solvents were investigated for their efficiencies as extractants for iodine. For this purpose standard potassium dichromate was used to obtain a standard quantity of iodine.

The three isomeric xylenes, toluene, *para*-cymene, cumene and other solvents were tested for their ability to extract iodine completely from the water solution, for their sensitivity (in absorbance) to small changes in iodine concentration, for their retention of constant absorbance over the longest period of time, and for their blank.

The absorption curves for 30 milliequivalents iodine (equivalent to 168 microliters oxygen) in 25 ml of selected solvents are shown in Fig. 2. The absorbance of iodine in each of these solvents exhibited a characteristic peak at 490 to 500 millimicrons.

Of the three solvents giving the highest absorbance with iodine, *meta*-xylene, cumene and *ortho*-xylene, two were unsatisfactory. Cumene and *meta*-xylene gave erratic results.

Iodine in *ortho*-xylene had the highest intensity and *ortho*-xylene showed a low blank. In addition, the color produced by the iodine was more stable, remaining unchanged for at least four hours. The absorbance of

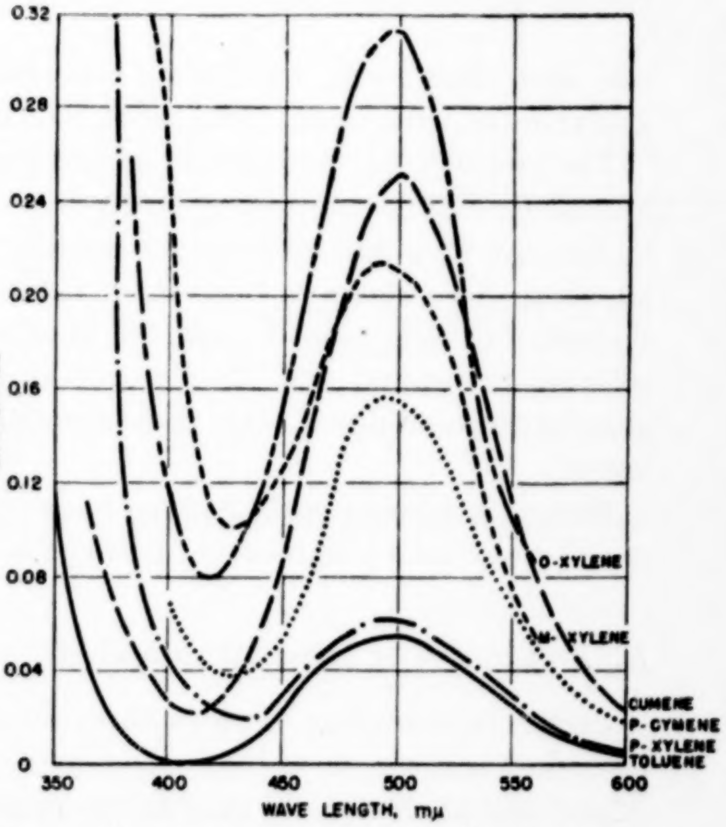

Fig. 2. Absorption curve of iodine in various solvents (30 ml 0.001N $K_2Cr_2O_7$, 25 ml solvent).

zero to 60 μl iodine (0 to 30 μl oxygen) in 25 μl solvent is shown for three solvents in Fig. 3.

The difference between the absorbance of iodine in *ortho*-xylene and that in toluene does not, of course, appear as great in the lower range as it does in the higher range (Fig. 2); but the blanks produced by toluene and by *para*-xylene are higher than those produced by *ortho*-xylene. In this particular experiment the blank for toluene was equivalent to 13 ppm of oxygen and for *para*-xylene 17 ppm of oxygen; while the blank for *ortho*-xylene was equivalent to just 3 ppm of oxygen.

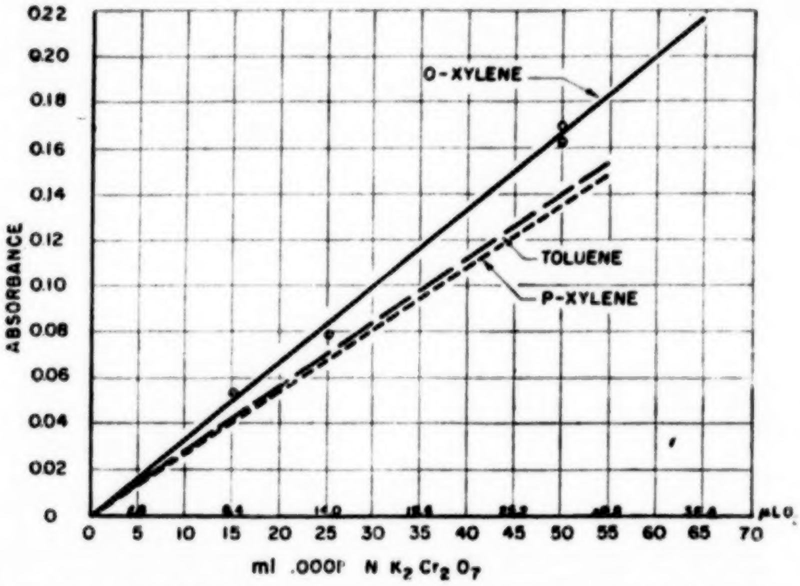

Fig. 3. Absorption of small amounts of iodine in various solvents (25 ml solvent, wave length 495 mμ).

Other solvents tried were benzene, 2,2,4-trimethylpentane and cyclohexane, but these gave low and erratic results. The more common solvents for iodine, carbon tetrachloride and chloroform, have been reported by PEPKOWITZ as giving even lower absorbances with iodine than does toluene.

The stability of the color of iodine absorbed in *ortho*-xylene was also tested. If water droplets containing oxidizable potassium iodide are allowed to remain in contact with the *ortho*-xylene solution, the *ortho*-xylene solution darkens on standing. To overcome this effect, the solution is filtered through filter paper. Exposure to light tends to fade the color. Consistent results are obtained when the solution is filtered and then stored in a dark cupboard until convenient for absorbance readings. Under these conditions the color is stable for at least four hours.

Many samples of *ortho*-xylene from different sources have been used. Only one of these had a high blank, perhaps having been aerated during manufacture.

B. Preparation of standard curves

Curves representing known quantities of oxygen were set up as follows: (The procedure is the same as that used for oxygen determination except that standard potassium dichromate is used as the standard oxidizing agent).

The absorbance of known quantities of iodine in 10 ml of *ortho*-xylene is shown in Fig. 4. The curve follows Beer's law, at least to 25 ppm (μ liters per liter) oxygen, when extracted into 10 ml of *ortho*-xylene, and to 50 ppm when extracted into 25 ml of *ortho*-xylene (Fig. 3). Fig. 5 shows that the quantity of iodine which may be extracted can be extended to 30 milliequivalents, a quantity equal to 168 ppm oxygen, by extracting into 50 ml of *ortho*-xylene. Above this point results are unreliable.

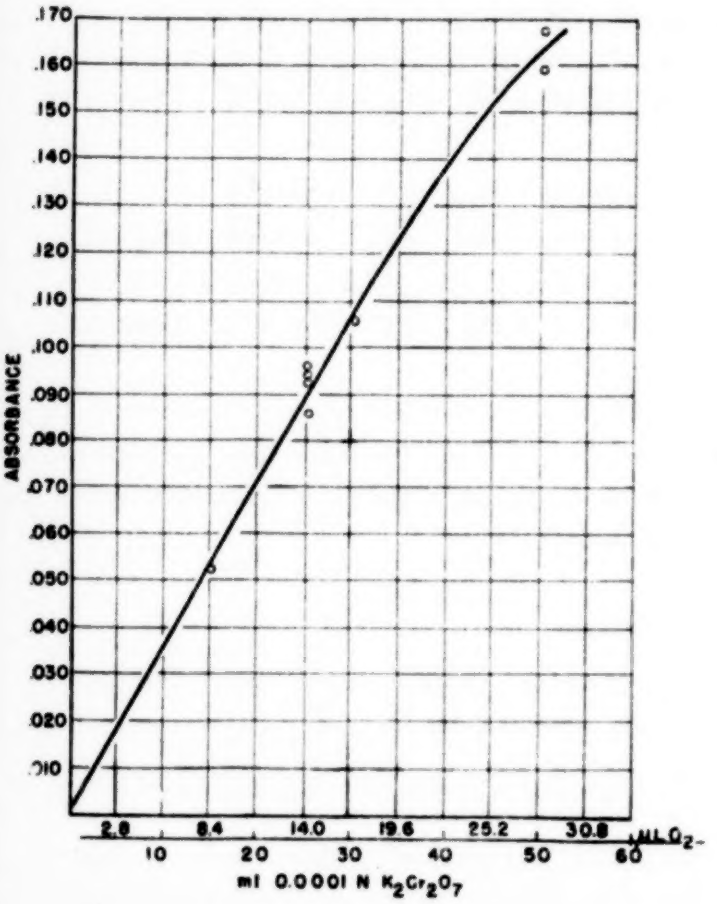

Fig. 4. Absorption of iodine in 10 ml *o*-xylene (equivalent to 0-20 μl oxygen).

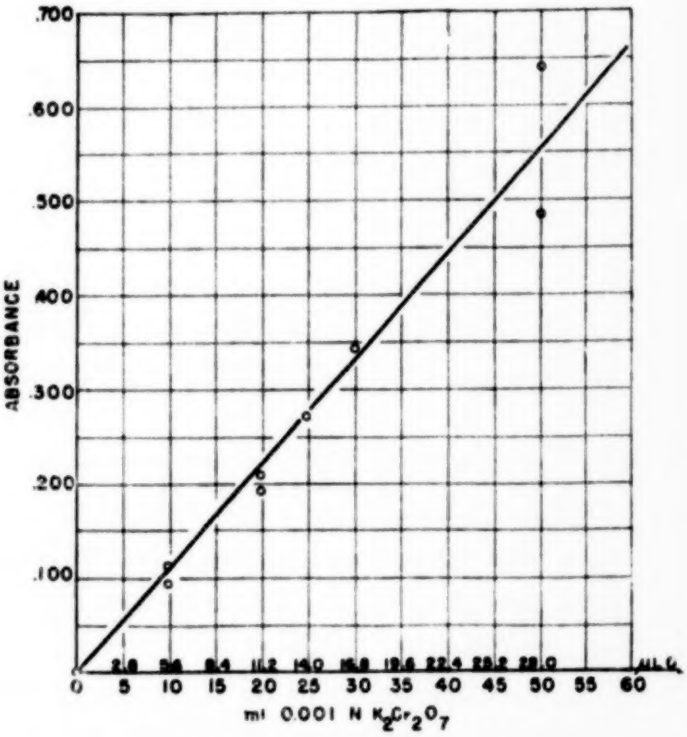

Fig. 5. Absorption of iodine in 50 ml *o*-xylene.

The equivalent oxygen-volume obtained from the standard dichromate solution is calculated as follows:

$$\mu\text{l of } O_2 = \frac{N \text{ of } K_2Cr_2O_7 \times \text{ml of } K_2Cr_2O_7 \times 22.4\cdot10^3}{4} \quad \ldots\ldots\ldots (1)$$

The color of the manganous-manganic precipitate is indicative of the iodine content and can be used as a criterion to determine the volume of *ortho*-xylene that will be required to extract all the iodine. The color ranges from nearly white for low iodine concentrations to brown for higher iodine concentrations. With experience the operator can estimate in which range the iodine concentration of a particular sample lies and select the correct amount of solvent to use.

C. Preparation of manganous solution

Previous experimentation had shown that manganous chloride in hydrochloric acid solution absorbs chlorine gas in the cold and releases the gas completely when hot. We applied this principle to the reduction of manganic ion, by boiling the solution (which was slightly acidified with hydrochloric acid), while purging it with carbon dioxide gas.

The manganous concentration chosen (20 mg/ml) is approximately that recommended by VAN STRATEN[8] for maximum oxygen absorption. A smaller aliquot of this solution, 25 ml (instead of VAN STRATEN's 100 ml) was chosen in order to reduce the volume of liquid in the liter reaction flask; the volume of oxygen being absorbed is relatively small in this procedure.

The effects of various treatments of the manganous solution are shown in Table I. Best results are obtained when the slightly acidic manganous chloride solution is freshly heated to boiling with carbon dioxide purging, cooled with continued purging and then added directly to the reaction flask.

D. Treatment of alkaline potassium iodide solution

Experimentation with the manganous-potassium iodide solution indicated that the alkaline potassium iodide solution would have to be specially prepared in order to obtain a low reproducible blank. Attempts to purify this reagent are summarized in Table II.

A low blank (1 ppm) was obtained when the potassium iodide and sodium hydroxide solutions were made up separately in boiled water and purged with carbon dioxide. Unfortunately, the reagent prepared in this way contained too much carbonate and would no longer react stoichiometrically with oxygen.

A fairly low blank (2.5 ppm) with little deviation (0.2 ppm) is obtained when the sodium hydroxide is separately dissolved in boiled water and purged with helium and the potassium iodide is separately dissolved in boiled water and purged with carbon dioxide. The solutions were freshly prepared each day.

E. Selection of vacuum grease

Several vacuum greases were tested for susceptibility to leaks (mechanical and thermal flow) and for their effect on the blank. The only satisfactory grease was one supplied by Consolidated Engineering of Pasadena, California. Apiezon grease, commonly used for vacuum work, is partially soluble in *ortho*-xylene and the resultant yellow color is significant in the zero to 10 parts per million oxygen range.

F. Gases with low oxygen concentration

A selection of gas samples obtained from compressed gas cylinders was tested for oxygen concentration to check the precision of the method (Table III). A standard deviation of 0.36 to 0.70 ppm was obtained for samples ranging from 2 to 23 ppm. The results were reproducible from day to day.

TABLE III

ANALYSIS OF VARIOUS GASES OF LOW OXYGEN CONCENTRATION

Gas analysed	Oxygen in ppm (μl/l)			
	Individual analyses		Average value	Standard deviation
	Date determined	Results		
Argon	12/16	23.7	23.1	0.7
	12/16	23.3		
	12/15	22.4		
Carbon dioxide	11/17	2.14	2.42	0.70
	11/17	1.93		
	11/18	2.77		
	11/19	1.77		
	11/19	3.47		
Helium	11/9	23.6	23.4	0.7
	11/16	22.6		
	11/16	24.0		
Hydrogen	11/30	2.94	2.73	0.36
	11/30	3.01		
	12/2	2.23		

In this low range the concentration of oxygen has no noticeable effect on precision. The average deviation is 0.615 ppm. The probably error according to "Student's test"[11] is 0.44 ppm (14–4 = 10 degrees of freedom). There is 95 per cent fiducial probability that any deviation will be less than one ppm. Reproducibility (99 per cent confidence-level) is 1.24 ppm.

A series of gas samples submitted to this laboratory were tested in duplicate (Table IV). The standard deviation was calculated for each set of duplicates[11]. The mean standard deviation is ± 0.33 with a 95 fiducial probability that any deviation is less than 0.55 ppm. Reproducibility (99 per cent confidence level) is 0.65 ppm. The larger standard deviation obtained from samples taken from gas cylinders is probably due to deviation in sampling rather than deviation in the analytical technique itself.

The results obtained for the helium gas samples are higher than desirable for use as industrial inert gas blankets which must be oxygen-free. C. HAMILTON (at this laboratory) showed that the oxygen concentration of this tank helium may be reduced to 3.5 ppm by passing the helium gas over uranium turnings at 600° C; similarly the oxygen concentration of a helium gas sample was reduced from 13 ppm to 3 ppm by W. HALLETT (at this laboratory) by passing the gas through liquid sodium.

TABLE IV

DUPLICATE ANALYSES OF GAS SAMPLES

Sample	Oxygen in ppm (μl/l) Individual analysis	Oxygen in ppm (μl/l) Average value	Standard deviation
1	1.9 1.3	1.6	±0.38
2	2.1 2.0	2.04	±0.08
3	4.2 4.5	4.35	±0.23
4	6.6 6.3	6.5	±0.23
5	7.8 8.4	8.1	±0.42
6	10.9 10.5	10.7	±0.28
7	16.6 16.0	16.3	±0.40
8	17.3 18.0	17.6	±0.53
9	28.1 27.3	27.7	±0.57
10	30.3 30.1	30.2	±0.14

It was also shown that the oxygen concentration of hydrogen gas could be reduced to 0.5 ppm, as analysed by the method described. This analysis, checked by the BRADY[2] method (apparatus calibrated with known quantities of oxygen) showed 0.4 ppm.

In another series, selected tanks of helium and hydrogen gas containing 6.6 and 2.7 ppm of oxygen, respectively, according to the procedure described, compared to 6.7 and 2.7 ppm respectively, by the BRADY method.

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G. Gases with high oxygen contents

When gas samples contain amounts of oxygen so great that they can no longer be determined by the proposed colorimetric method, the aqueous potassium iodide solution can be titrated with standard sodium thiosulfate solution. In this event the *ortho*-xylene extraction step is, of course, omitted.

In this upper range, however, the manganese-reagent concentration is critical. The maximum amount of oxygen which can be determined by the proposed method is limited by the capacity of the manganous solution to absorb oxygen. A large excess of manganese is not to be used since, according to VAN STRATEN[8] and TAYLOR AND ALEXANDER[7] such excess inhibits oxygen absorption. VAN STRATEN's procedure is suggested.

Two brands of dry nitrogen which contained high oxygen contents were tested (Table V). A specific sample of Airco dry nitrogen was analysed both by extraction into *ortho*-xylene and by titration with sodium thiosulfate. The results were beyond the planned range of the procedure (greater than 2000 ppm). Analysis of smaller samples (90 to 150 ml) indicated the oxygen concentration was still out of range of this procedure (greater than 5000 ppm).

TABLE V

ANALYSIS OF HIGHER CONCENTRATIONS OF OXYGEN IN DRY NITROGEN

Brand	Sample size (ml)	Oxygen in ppm (μl/l)		
		Individual analyses	Average value	Standard deviation
Airco	275—500	>2000 a >2000 b	—	—
Airco	90—150	—	>5000 a,b	—
Linde	166	2120 a	2106	36
	133	2110 a		
	109	2140 a		
	85	2055 a		

a. Estimated from a dilution of the *o*-xylene extraction.
b. Titrated with sodium thiosulfate.

A second brand, Linde dry nitrogen, contained oxygen in concentration low enough for this procedure. The average of four determinations was 2106 ppm with a standard deviation of 36 ppm (a deviation of less than 2%).

DISCUSSION

A study of the modifications of the WINKLER methods currently used for the determination of small amounts of oxygen (1 part per million or more) emphasized the fact that all reagents used must be completely de-aerated in order to obtain a low, reproducible blank in the parts per million range. Furthermore, the analytical system must be kept isolated from air until the free iodine (liberated) is extracted into an organic solvent. This is made possible by conducting the entire analysis in vacuum when determining small amounts of oxygen with accuracy.

Among the many solvents tested, *ortho*-xylene offers the highest absorbance with iodine, the most stable color, and a low reproducible blank.

Using the proposed vacuum-type procedure, from one to thirty parts per million oxygen can be determined with a mean standard deviation of ± 0.33 ppm with a 99 per cent fiducial probability that any deviation will be 0.75 parts per million or less.

The upper working limit is 2,000 ppm of oxygen in a 200-ml sample. The sample size must be reduced and the quantity of manganese solution increased, if the oxygen content is above this concentration; the iodine-thiosulfate titration is recommended instead of the colorimetric method. In this range the deviation is expected to be less than two per cent.

The accuracy of the method compares favorably with that of BRADY[2]. Tank gases analysed by either method gave results within 0.1 ppm of each other.

APPENDIX

Method summary

A sample of gas, measured by volume-pressure relationships, is shaken with a freshly prepared suspension of manganous hydroxide and potassium iodide in aqueous medium. The manganous hydroxide is oxidized to the manganic stage by oxygen. Upon acidification the manganic ion oxidizes iodide ion to free iodine. The iodine is extracted into *ortho*-xylene and determined spectrophotometrically.

Apparatus

The apparatus is shown in Fig. 1. The vacuum system is evacuated by a Duo Seal Vacuum pump and the evacuated pressure is read by means of a thermocouple gauge. The entire system is demountable, with ball and socket joints interjected between each piece of apparatus so that the various parts may be readily disassembled and reassembled.

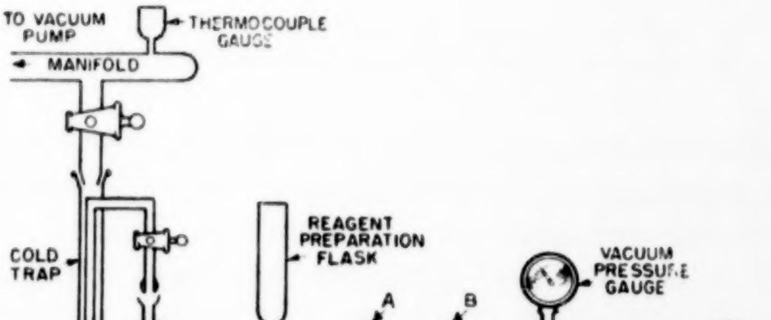

Fig. 1. Schematic of apparatus for determination of oxygen in certain gases.

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The system is evacuated through a cold trap which is immersed in liquid nitrogen to collect moisture and vapor from organic solvents. A preliminary trap catches the majority of the moisture.

The "reagent preparation flask" is used to prepare the manganous chloride solution, the hydrochloric acid solution and to add reagents to the reaction flask. The reagent preparation flask contains a special three way stop-cock, the bore of which can be readily evacuated.

The reaction flask is provided with a side arm to facilitate mixing and to introduce the alkaline potassium iodide solution. Vacuum stop-cocks are used to minimize the possibility of leakage.

The vacuum-pressure gauge is used to read the sample pressure. The test sample is introduced from a sample bulb, Fig. 6, which has two stop-cocks, a vacuum stop-cock to minimize the danger of leakage and a three-way stopcock to facilitate the sampling operation.

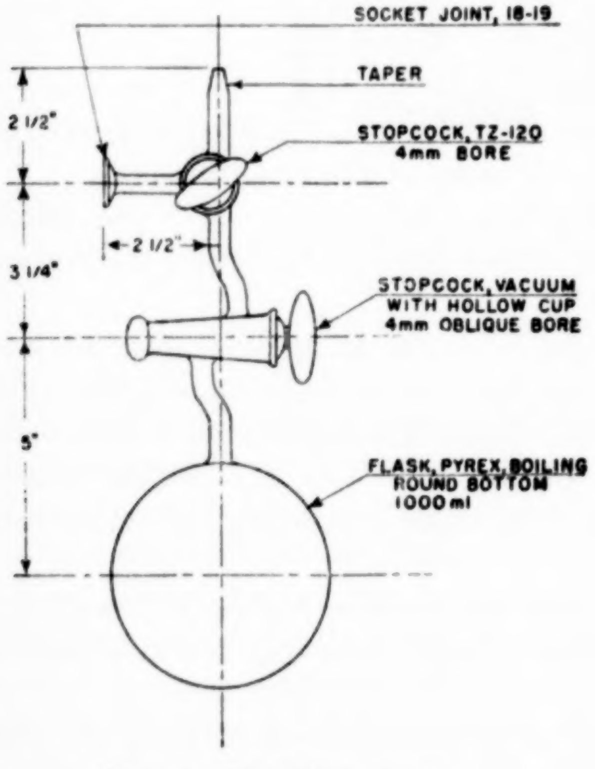

Fig. 6. Sampling bulb.

A specially designed mixer, shown in Fig. 7, is used to rotate the reaction flask in order to mix the gaseous sample and the absorbing solution. Two reaction flasks are clamped to a shaft, which is rotated by a pulley driven by an electrical motor. The speed of the motor is adjusted by a Variac so that the flasks turn at a rate of about five revolutions per minute; this slow circular motion provides maximum mixing of the sample gas and absorbing solution.

A resistance heater is used to heat the solutions in the "reagent preparation flask". This consists of a length of wire, imbedded in a ceramic molded to fit the flask. The temperature of the heater is controlled by a Variac.

PREPARATION OF SOLUTIONS

0.3N potassium iodide

Heat 100 ml of distilled water to boiling in a 200-ml boiling flask with carbon dioxide purging. Remove the flask from the heat and cool with continued purging. Add 5 g potassium iodide and dissolve by swirling the contents of the flask. Cool to room temperature with continued carbon dioxide purging. Prepare daily.

1.5N sodium hydroxide

Heat 100 ml of distilled water to boiling with helium purging in a 200-ml boiling flask. Cool the flask with continued purging. Weigh 6 g of sodium hydroxide and add immediately to the boiled water. Dissolve the pellets with swirling and continue helium purging until the solution is cooled to room temperature. Prepare daily.

0.1M manganous chloride

Dissolve 10 g of $MnCl_2.4H_2O$ in 500 ml distilled water which has been slightly acidified with hydrochloric acid. Heat to boiling, with carbon dioxide purging, and continue boiling from 5 to 10 minutes. Cool with continued purging. Dilute to 500 ml with boiled, purged water.

Analysis of gas sample

Assemble the system as is shown in Fig. 1, using a Consolidated grease of suitable temperature range, omitting the side arm of the reaction flask.

Pipette 10 ml of 1.5*N* sodium hydroxide solution and 5 ml of 0.3 *N* potassium iodide solution into the side arm. Put the side arm in place and evacuate the system to less than 3 microns.

While the system is evacuating, pipette 25 ml of the manganous chloride into the reagent preparation flask, pipetting carefully to exclude air bubbles. Put the circular heater in place around the flask. Bring the solution to a boil while purging it with carbon dioxide. Remove the heater. Cool the solution with a jet of air directed against the outside of the flask while continuing carbon dioxide purging.

When the manganous solution is cool and the system has been evacuated, suck the manganous solution into the reaction flask, reserving the last portion of the solution to prevent air leakage.

Check the evacuated pressure of the system. Close stop-cock A of the reaction flask and open the stop-cocks of the sample bulb to permit the sample gas to flow into the reaction flask. Measure the sample pressure and record the room temperature.

Close stop-cock B. Disassemble part of the system up to the reaction flask and place the reaction flask on the mixer (Fig. 7). Agitate the mixture at about 5 revolutions per minute for two hours.

Re-insert the reaction flask in the vacuum system, in the reverse direction, so that stop-cock B is now closest to the vacuum pump. Re-evacuate the system, except the reaction flask, to less than 3 microns.

While evacuating, pipette 20 ml of boiled, purged, distilled water and 5 ml of concentrated hydrochloric acid into the reagent preparation flask. Heat to boiling with carbon dioxide purging. Cool with continued purging.

When the hydrochloric acid solution is cool, suck it into the reaction flask without permitting the entry of air. Add 10 ml of *ortho*-xylene through the reagent flask to the reaction flask without permitting the entry of air.

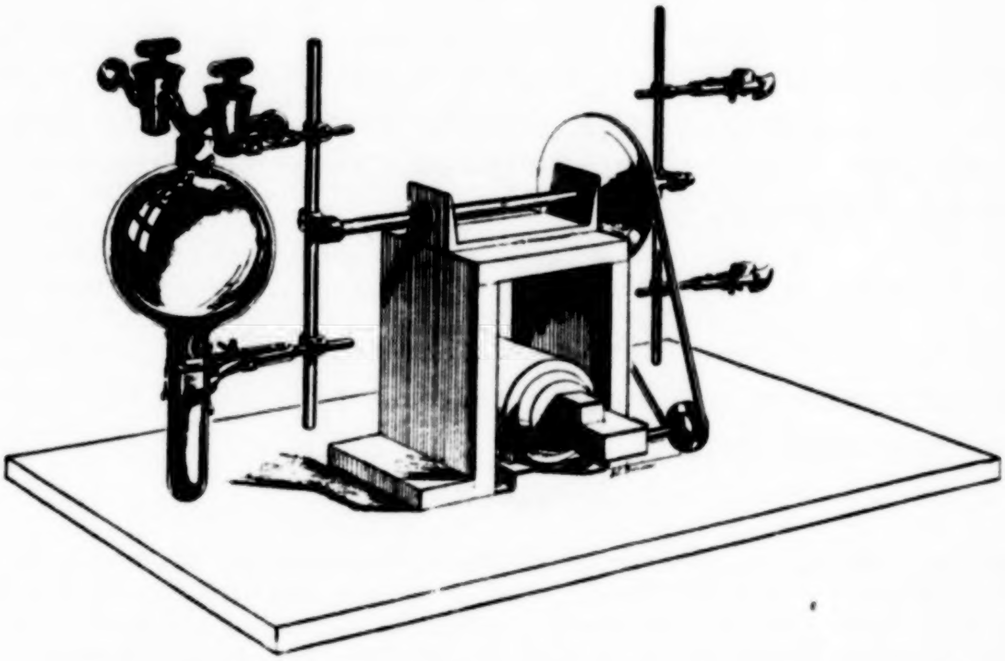

Fig. 7. Mixer (determination of oxygen in certain gases).

Close the stop-cocks, remove the reaction flask and extract the iodine into the *ortho*-xylene with gentle shaking to prevent the formation of an emulsion. When the extraction is complete the aqueous layer will be water white.

Open the flask to the atmosphere, drain out the liquid, and separate the two layers. Filter the organic layer through paper into a 10-ml volumetric flask. Dilute to volume with *ortho*-xylene. Store the solution in the dark until ready to read spectrophotometrically. Read the sample at 495 millimicrons within the next four hours, using a Beckman, Model DU, spectrophotometer.

Calculate the volume of the gas sample from the universal gas laws.

$$V_s = V \times \frac{273}{T} \times \frac{P}{760}$$

where V_s = Volume of the gas sample at standard conditions
V = calibrated volume of the reaction flask corrected for volume of absorbing solution
T = room temperature in degrees Kelvin
P = sample pressure in mm mercury (corrected for vapor tension)

Convert the spectrophotometric reading to ml of standard dichromate, using a standard curve such as is shown in Fig. 4, and calculate the oxygen equivalent, according to equation (1):

$$\mu \text{ liters of } O_2 = \frac{N \text{ of } K_2Cr_2O_7 \times \text{ml of } K_2Cr_2O_7 \times 22.4.10^3}{4} \quad \ldots\ldots \quad (1)$$

or (1 ml of $0.0001N$ $K_2Cr_2O_7 = 0.56$ μl O_2 in the 10 ml *o*-xylene extract
$= 0.22$ μl O_2 in the 25 ml *o*-xylene extract)

Finally, calculate "oxygen, ppm" by dividing micro-liter oxygen by the calculated volume of gas sample.

ACKNOWLEDGEMENT

The mechanical apparatus was designed and built by WILLIAM TAYLOR.

SUMMARY

An improved method is described for the determination of micro-amounts of oxygen gas in argon, carbon dioxide, helium, hydrogen and nitrogen by the WINKLER procedure. The technique is such that a mean standard deviation of ± 0.33 ppm oxygen with a reproducibility of ± 0.67 is obtained for gases varying in oxygen content from 1 to 30 ppm. The results are reproducible on a day-to-day basis. The reagent blank is equivalent to about 2.5 ppm with a deviation of 0.2 ppm. The method can be used for oxygen gas determination from 1 to 150 ppm. The accuracy of the method is ± 0.1 ppm for the lower range of oxygen concentrations.

The method may also be extended to higher oxygen-containing gases, except that the oxygen determination is made by titration and smaller gas samples are used.

RÉSUMÉ

Une méthode est décrite pour le dosage de micro-quantités d'oxygène dans l'argon, l'anhydride carbonique, l'hélium, l'hydrogène, et l'azote par le procédé de WINKLER.

La technique est telle qu'on peut obtenir une déviation standard moyenne de ± 0.33 p.p.m. d'oxygène avec une reproductibilité de ± 0.67 pour des teneurs en oxygène allant de 1 à 30 p.p.m. Les résultats sont reproductibles. L'essai à blanc donne environ 2.5 p.p.m. avec une déviation de 0.2 p.p.m. Cette méthode peut être utilisée pour doser des quantités d'oxygène allant de 1 à 150 p.p.m. La précision est de ± 0.1 p.p.m. pour les plus faibles teneurs en oxygène. Cette méthode peut être appliquée à des gaz plus riches en oxygène, en effectuant alors le dosage par titration et en utilisant des prises de gaz plus petites.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben über die Bestimmung von kleinsten Mengen von Sauerstoff in Argon, Kohlendioxyd, Helium, Wasserstoff und Stickstoff nach der Methode WINKLER. Nach der genannten Technik kann man eine mittlere Standardabweichung erhalten von ± 0.33 p.p.m. Sauerstoff mit einer Reproduktibilität von ± 0.67 für einen Gehalt an Sauerstoff von 1 bis 30 p.p.m. Die Resultate lassen

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sich reproduzieren. Der Blindversuch gibt ungefähr 2.5 p.p.m. mit einer Abweichung von 0.2 p.p.m. Diese Methode kann verwendet werden, um Sauerstoffmengen von 1 bis 150 p.p.m. zu bestimmen. Die Präzision ist für die kleinsten Mengen von Sauerstoff ± 0.1 p.p.m. Diese Methode kann auch für Gase, welche reicher an Sauerstoff sind, verwendet werden, indem man die Bestimmung durch eine Titration vornimmt und indem man über kleineren Mengen Gas arbeitet.

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THE CHROMATOGRAPHIC SEPARATION OF A MIXTURE OF THE CHLORIDES OF CALCIUM, STRONTIUM, BARIUM AND MAGNESIUM

by

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BURSTALL *et al.*[1] have separated the alkaline earth chlorides on paper chromatograms using pyridine containing 20% water and 1% potassium thiocyanate as solvent, and alizarin and sodium rhodizonate as spray reagents. Similarly ERLENMEYER *et al.*[2] have studied the separation of the alkaline earth acetates employing a solvent mixture of ethanol containing 20% of 2*N* acetic acid, violuric acid being used to locate the position. Strontium and barium have also been separated by MILLER AND MAGEE[3] employing butanol-conc. HCl saturated with *n*-butyl chloride. In the present note, alkaline earth chlorides (including magnesium) were separated on circular discs, following GIRI AND RAO'S[4] modification of RUTTER'S[5] technique, with mixed alcohols as solvents. A number of solvent mixtures were tried, of which solvents containing methanol as one of the constituents were found to give the best results. Mixture of indophenol dye and silver nitrate was used to detect the chlorides on the chromatogram.

MATERIALS AND REAGENTS

Paper: Whatman filter paper No. 1 discs (24 cm diameter)

Solvents: Mixtures of ethanol and methanol (1 : 1), *iso*propanol and methanol (2 : 3), butanol and methanol (3 : 7) and pentanol and methanol (3 : 7) were separately used.

Spray reagent: 2, 6, dichlorophenolindophenol (0.2 g) in ethyl alcohol (100 ml), to which silver nitrate (3 g) was added and filtered. The spray reagent was prepared before use.

METHOD AND RESULT

A circular paper disc (24 cm) was spotted with 10 μl of aqueous solutions of the chlorides containing approximately 200 μg of test substance per spot, and was developed in a circular trough (26 cm diameter) in the manner suggested by

GIRI AND RAO (*loc. cit.*). The chromatogram after development, was air-dried and treated with the spray reagent. On drying, the chlorides developed faint pink bands, which on exposure to sunlight turned intense brown.

The above-mentioned solvents were successful in bringing about the separation of the chlorides of calcium, strontium, barium and magnesium. A typical chromatogram using ethanol-methanol mixture is given below, the R_F values obtained being Mg(0.80), Ca(0.62), Sr(0.49) and Ba(0.28).

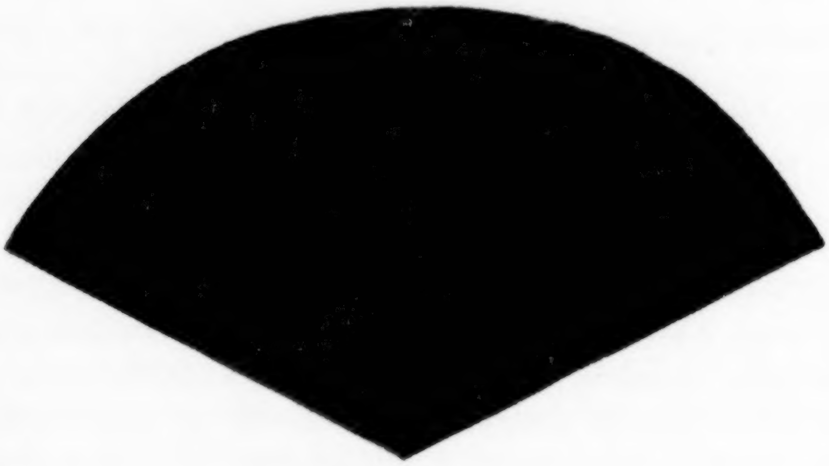

Fig. 1. A circular paper chromatogram showing the separation of the chlorides of calcium, strontium, barium and magnesium.

SUMMARY

The chlorides of calcium, strontium, barium and magnesium have been separated on circular paper, using mixed alcohols, containing methanol as one of the constituents, as solvents. Approximate R_F values obtained by using ethanol containing 50% methanol, have been reported.

RÉSUMÉ

Les auteurs décrivent une séparation: calcium, strontium, baryum et magnésium (sous forme de chlorures) sur papier circulaire. On utilise comme solvant un mélange d'alcools (renfermant entre autres le méthanol). Des valeurs approximatives de R_F, obtenues avec l'éthanol renfermant 50% de méthanol, sont données.

ZUSAMMENFASSUNG

Die Chlorverbindungen mit Kalzium, mit Strontium, mit Barium und mit Magnesium hat man auf einem kreisförmigen Papier getrennt, wobei gemischte Alkohole, die das Methanol als eines der Bestandteile enthalten, als Lösungsmittel verwendet worden. Annähernde Werte, die man dadurch erhält, dass man im Ethanol, das 50% Methanol enthält, verwendete, wurden angegeben.

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THE SEPARATION OF MERCURY FROM GOLD BY ION EXCHANGE

by

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The use of ion-exchange resins to separate mercury from gold in large quantities simplifies an otherwise laborious task. Mercuric mercury and auric gold form complex ions, $HgCl_3^-$ and $AuCl_4^-$. The stability constants for these complexes according to LATIMER[1] are $K_{HgCl_3^-} = 8.3 \cdot 10^{-15}$ and $K_{AuCl_4^-} = 5 \cdot 10^{-22}$.

On the basis of this information it was predicted that a chloride ion concentration could be selected which would convert a minimum of mercuric ion and a maximum of auric ion to the corresponding complexes. Thus it was anticipated that mercury could be maintained largely as a cation while the gold was converted to an anion. Under these conditions it was predicted that mercury could be retained by a cation exchange resin while gold would pass through the column as an anion. This predicted arrangement also fitted the practical aspects of the problem since the gold was present in large amount compared with the mercury (50:1) and less resin, a smaller column and less time would be needed if mercury was to be retained rather than gold.

Against the probability of this idea working was a statement by NOYES AND BRAY[2] that the reason why mercury rather than gold can be extracted from ethyl acetate with aqueous 3*N* ammonium chloride is the strong complexing tendency of mercuric and chloride ions. It would be inferred from this statement that the mercuric complex is much stronger than the auric complex which however does not seem to be the case.

From previous experience[3] in this laboratory it seems that the resin Dowex 50, made by the Dow Chemical Co., Midland, Michigan, would serve for this separation. Preliminary experiments with a small portion of solution containing mercuric and auric chlorides in 2*N* hydrochloric acid indicated a satisfactory separation could be made. Tests for mercury by precipitation with iodide were made on the eluate and the capacity of the resin estimated at about 10 mg of mercury per gram of resin. The eluate was also examined spectroscopically and no lines could be determined for any other metals than gold.

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A large column containing about 800 grams of Dowex 50 was then prepared. The column consisted of a Pyrex tube 100 cm long × 55 mm diameter. It was fitted at the lower end with a stopcock and was mounted in a vertical position. A wad of glass wool was added to support the resin. The resin was first soaked in 2*N* hydrochloric acid overnight in order to convert it from the sodium form to the hydrogen form and also to allow for any expansion due to hydration. The resin was then transferred to the column and washed with distilled water until the pH of the eluate rose to 5. The resin was kept covered with water at all times.

The main gold solution consisted of 1800 ml of a 2*N* hydrochloric acid solution containing about 400 grams of gold and 8 grams of mercury. It was poured onto the column and the elution rate adjusted to 10 ml per minute. The eluate was collected in 100 ml portions and tests for mercury were made with iodide on each portion. None was detected. After all of the gold solution had been added to the column, water was used to elute the gold until yellow color was no longer apparent. Approximately 1500 ml was required. Mercury could not be detected by the iodide test in any of the 100 ml portions of wash eluate. Finally all of the 100 ml portions were combined and examined spectroscopically by emission spectra. Neither mercury nor any other metals could be detected by this means.

The whole process for this quantity of gold takes less than 6 hours and requires only occasional attention from the operator. The mercury can be displaced from the column with 2*N* hydrochloric acid. The resin can be regenerated in this way and used over again.

SUMMARY

Mixtures containing large amounts of gold and small amounts of mercury (50:1) can be quantitatively separated by passing a 2*N* hydrochloric acid solution of the chlorides through Dowex 50 resin. Mercury behaves as a cation and is quantitatively retained. Gold behaves as an anion and is not retained by the resin. The gold is obtained spectroscopically free from all metals. The capacity of the resin is approximately 10 mg of mercury per gram of resin. The resin is freed from mercury by washing with 2*N* hydrocloric acid and may be used over again.

RÉSUMÉ

De grandes quantités d'or, en présence de faibles quantités de mercure (50:1), peuvent être quantitativement séparées par passage de leurs chlorures en solution acide chlorhydrique 2*N*, à travers la résine Dowex 50. Le mercure se comporte comme un cation, il est retenu quantitativement. Par contre, l'or agit comme anion et n'est pas retenu par la résine. L'or ainsi séparé est spectroscopiquement exempt de tous métaux. La capacité de la résine est approximativement de 10 mg de mercure par gramme de résine. La résine est débarrassée du mercure par lavage à l'acide chlorhydrique 2*N* et peut être utilisée à nouveau.

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ZUSAMMENFASSUNG

Mischungen, die grosse Mengen von Gold und kleine Mengen von Quecksilber enthalten (50 : 1), können mengenmässig getrennt werden, indem man eine 2*N* Salzsäurelösung der Chloride durch Dowex 50 Harz führt. Quecksilber ist dabei als ein Kation wirksam und wird mengenmässig zurückbehalten. Gold wirkt als Anion und wird vom Harz nicht zurückbehalten. Das Gold erhält man spektroskopisch frei von allen Metallen. Die Aufnahmefähigkeit des Harzes ist ungefähr 10 mg Quecksilber pro Gramm Harz. Das Harz wird durch 2*N* Salzsäurewäsche vom Quecksilber freigemacht und kann wieder benützt werden.

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THE PHOTOMETRIC DETERMINATION OF COBALT BY EXTRACTION WITH β-NITROSO-α-NAPHTHOL

by

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INTRODUCTION

β-Nitroso-α-naphthol was introduced in 1919 by BELLUCCI[1] as a colorimetric reagent for the estimation of cobalt. YOE AND BARTON[2] described a photometric procedure in which the cobalt complex was developed in an ammoniacal citrate solution; this method was subject to interferences by nickel, copper, manganese and large amounts of iron. The first extraction procedure (by benzene) was described by CARDINI, JUNG AND FUKSMAN[3]. Recently BARON[4] published a method especially adapted to the determination of traces of cobalt in fodder and soil. The effect of a large number of elements in 5 mg quantities was investigated and his method proved to be highly selective and sensitive.

As, in our opinion, there is a need for a sensitive extraction method for the determination of cobalt in ferrous and non-ferrous alloys, we decided to investigate BARON's method from this point of view.

EXPERIMENTAL

In the procedure as given by BARON, the sample solution, containing citrate and about 5% by volume of acetic acid, is heated at 90° with 1 ml of a 1% reagent solution in concentrated acetic acid. After cooling, the solution is extracted with toluene, causing the cobalt complex and the excess reagent to pass into the organic phase. By shaking the toluene with $2N$ sodium hydroxide the excess reagent passes into the aqueous layer, leaving the cobalt complex in the toluene. The optical density of the toluene solution is then measured at a wavelength of about 530 mμ.

Because of the inflammability of toluene we preferred the use of chloroform for the extraction; this proved to be as suitable as toluene.

Influence of iron

When applying the above procedure to solutions containing large amounts of trivalent iron there was interference from a green precipitate of the ferrous nitrosonaphthol complex. This is due to the fact that in hot citrate solutions trivalent iron is partly reduced to the divalent state. An attempt was made to develop the cobalt complex in the cold. This complex, however, develops rather slowly at room temperature and a standing time of about 30 min was necessary for complete development. Even then a small amount of ferrous complex was always formed, probably by photochemical reduction. This could be prevented by the addition of a small amount of hydrogen peroxide, which did not interfere. With these modifications traces of cobalt could be determined in the presence of 1 g of iron.

Influence of pH

In citrate solution extraction by chloroform is complete in the pH range 2.5 to 5, when using 2 ml of reagent and extracting three times. A shaking time of 1 min by hand is sufficient, in contrast to BARON, who prescribes a shaking time of 5 min on a shaking machine. The addition of acetic acid or sodium acetate prescribed by BARON is unnecessary.

Amount of reagent

With 1 ml of reagent the extraction of cobalt quantities up to 200 μg was not always complete. Increasing the amount of reagent to 2 ml proved to be adequate for complete extraction.

Optimum wavelength

Maximum absorption of the cobalt complex in chloroform occurs in the wavelength region 520 to 540 mμ, with a relatively flat maximum at 530 mμ. At this wavelength 200 μg of cobalt in a volume of 50 ml chloroform give an optical density of 0.95 in a 1 cm cell. Beer's law is valid up to optical densities of 1 and above. All measurements were carried out with a Unicam SP500 spectrophotometer.

Stability of the colour

In accordance with BARON the colour was found to be stable for at least 12 hours.

Purity of reagent

In applying the recommended procedure to cobalt-free solutions it appeared that the chloroform showed a slight colour. With the best quality of reagent available (Merck, Darmstadt, zur Analyse) this blank was equivalent to about 1 μg of cobalt, when using a freshly made solution. On storing the reagent solution this blank increased by about 1 μg a day. Reagent samples from other sources showed much higher initial blanks (up to 10 μg). It was found that blanks of the order of a few tenths of a microgram could be obtained by shaking the reagent solution with activated carbon; this applies as well to fresh or aged solutions as to solutions made from impure reagent.

Influence of diverse elements

Determinations of 10 to 50 μg of cobalt in the presence of 100 mg of diverse elements according to the recommended procedure showed no interference from the following elements: Al, Sb(III and V), As(III and V), Ba, Be, Bi, B(as borate), Cd, Ca, Ce(III), Cr(III), F, Ga, Ge(as germanate), I(as iodide), Fe(III), La, Pb, Mg, Mn, Hg(II), Mo, Ni, Nb, P(as phosphate), Se(IV and VI), Si, Ag, Sr, Ta, Th, Ti, Tl(I)*, Sn(IV), W, U(VI)**, V(V), Zn, Zr.

Interferences

Although *gold* and *platinum* by themselves are not extracted, the presence of 1 to 2 mg of either of these elements leads to too high values for cobalt (error +5 to +10 μg Co). This is not in accordance with BARON, who reports no interference from 5 mg of gold.

Palladium, is extracted and interferes strongly. It can be easily removed by a chloroform extraction of the palladium dimethylglyoxime-complex from a dilute mineral acid solution. The excess dimethylglyoxime can be destroyed by boiling with nitric acid.

Divalent tin and *divalent iron* interfere, as already reported by BARON; any interference from these can be prevented by oxidizing the sample solution.

Nickel. In the presence of large quantities of nickel a nickel nitroso-naphthol complex is formed, giving a red precipitate in the aqueous solution, especially above pH 4. This nickel complex gathers in the chloroform and when shaken with 2*N* sodium hydroxide a thick chloroform emulsion is formed, making the cobalt determination impossible. When the reaction is carried out at a pH between 3 and 3.8 and the chloroform extract is first shaken with 2*N* hydrochloric acid, the nickel complex is decomposed and passes into the hydrochloric acid. After shaking the chloroform with 2*N* sodium hydroxide a normal cobalt determination is possible. It is however necessary to increase the amount of reagent in order to get complete extraction of cobalt in the presence of much nickel. Above 100 mg of nickel an extra addition of 2 ml of reagent for every 250 mg of nickel or less is adequate. In this way a few micrograms of cobalt could be determined in the presence of 1 g of nickel.

Copper up to 25 mg does not interfere, although a dark brown copper complex is formed, which is soluble in chloroform. This complex is destroyed by shaking with hydrochloric acid and sodium hydroxide. Evidently the copper complex consumes enough reagent to make the extraction of cobalt incomplete in the presence of large amounts of copper. Thus with 50 mg of copper and the quantity of reagent increased to 4 ml, the recovery of cobalt is about 90%; with 100 mg of copper and largely increased amounts of reagent the cobalt recovery is only of the order of 10%.

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* only 25 mg tested.
** only 50 mg tested.

It was possible to extract cobalt completely in the presence of 100 mg of copper by complexing the copper with a large excess of iodide and thiosulphate; if iron, however, is also present this is reduced and the ferrous complex interferes. The simplest method to determine cobalt in the presence of more than 25 mg of copper is to first separate the copper electrolytically.

Ammonium salts in large quantities (*e.g.* 5 g) give results which are somewhat low; 1 g of ammonium chloride did not interfere.

RECOMMENDED METHOD

Special solutions required.

Sodium citrate solution 40%. Dissolve 400 g sodium citrate, $Na_3C_6H_5O_7 \cdot 2\ H_2O$, in water and dilute to 1 liter.

Reagent solution. Dissolve 1.0 g β-nitroso-α-naphthol $C_{10}H_6NO \cdot OH$ in 100 ml concentrated acetic acid. Add 1 g of activated carbon. Shake the solution before use and filter off the necessary amount.

Chloroform, AR quality.

Procedure

Take a sample containing not more than 200 μg of cobalt in dilute acid solution in a 100 ml beaker, add sufficient 40% sodium citrate to keep 3- and 4-valent metals in solution, at least 10 ml (see note 3), dilute to 50-75 ml and adjust the pH in the range 3-4 by the addition of 2*N* hydrochloric acid or 2*N* sodium hydroxide, using pH paper as indicator. Cool to room temperature, add 10 ml 3% hydrogen peroxide and, after a short interval, 2 ml reagent solution. Stand the solution at least 30 min at room temperature. Transfer to a 125 ml separating funnel, washing the beaker twice with 5 ml chloroform, which are added to the solution in the separating funnel. Add chloroform to a total volume of about 25 ml and shake vigorously for 1 min. After complete separation of the layers draw off the chloroform into a 50 ml volumetric flask and repeat the extraction twice with 10 ml chloroform. Dilute the combined extracts to the mark with chloroform and mix thoroughly. Transfer the chloroform solution to a clean separating funnel*, add 20 ml 2*N* hydrochloric acid and shake 1 min. Draw off the chloroform into a separating funnel, add 20 ml 2*N* sodium hydroxide and shake 1 min. Draw off the chloroform into a separating funnel and again shake with 20 ml $2N$ sodium hydroxide for 1 min. Finally draw off the chloroform through a small plug of cotton wool in the stem of the funnel into an absorption cell, discarding the first few ml.

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* This need not be done quantitatively as the concentration of the cobalt complex in the chloroform is not changed by the following treatments .

Measure the optical density of this chloroform solution against pure chloroform at a wavelength of 530 mμ. Subtract the optical density of a blank carried through the whole procedure and determine the amount of cobalt from a previously prepared calibration curve.

Determine 20-200 μg of cobalt in a 1-cm cell
,, 10-100 μg ,, ,, ,, ,, 2-cm cell
,, 5- 50 μg ,, ,, ,, ,, 4-cm cell

Notes

1. Gold, palladium and metals of the platinum group interfere and should be absent.
2. Iron should be in the ferric state before the addition of citrate.
3. 10 ml of citrate solution is sufficient to keep about 350 mg of iron in solution. For the determination of cobalt in steel use 15 ml of citrate solution for a 0.5 g sample and 25-30 ml for a 1 g sample. On adjusting the pH with sodium hydroxide a precipitate of ferric hydroxide usually forms. This can be dissolved by heating the solution. If the solution is free from ammonium salts the neutralization can be carried out with ammonium hydroxide, which causes no precipitation of ferric hydroxide
4. Copper in excess of 25 mg interferes and should be removed.
5. In the presence of more than 100 mg of nickel the pH of the solution after the addition of the reagent should be between 3.0 and 3.8 and an extra addition of 2 ml of reagent should be made for every 250 mg of nickel or less.
6. Ammonium salts in excess of about 1 g give rise to slightly low results.
7. Calibration curves. Prepare a series of solutions containing 0, 5, 10, 20, 40, 60, 80, 100, 150 and 200 μg Co in a volume of about 50 ml and proceed according to the recommended procedure. Measure the solutions containing cobalt against the solution without cobalt in the appropriate absorption cells and plot optical density against amount of cobalt.

The procedure as given above has been applied to a number of standard samples with the results shown in Table I. The steel samples were dissolved in the acids normally used for these samples in steel analysis; the tungsten steels were dissolved in a mixture of sulphuric and phosphoric acids and fumed after the addition of nitric acid. When more than one determination was made, these were carried out by different analysts.

In order to test the procedure for the determination of traces of cobalt in nickel a sample of very pure nickel was obtained and the cobalt content determined by extraction with tetraphenylarsoniumchloride according to AFFSPRUNG, BARNES AND POTRATZ[5]. This was found to be $6 \cdot 10^{-4}\%$. With our procedure, using 0.5 and 1 g samples also $6 \cdot 10^{-4}\%$ Co was obtained. Microgram additions of cobalt to 1 g samples of this nickel were recovered completely.

TABLE I

Sample No. NBS = National Bureau of Standards BCS = British Chemical Standard		Sample weight or aliquot	Certified value and range % Co	Co found %
NBS 101a	18Cr-8Ni steel	150 mg	0.070 (0.060—0.080)	0.076
NBS 115	Cu-Ni-Cr cast iron	40 mg	0.08	0.08
NBS 126a	High-nickel steel (35.9 % Ni)	7.5; 20 mg	0.30 (0.29—0.32)	0.31; 0.30; 0.30; 0.30
NBS 153	Co-Mo-W-steel (1.58 % Mo; 8.4 % W; 4 % Cr; 2 % V)	0.6; 1.0 mg	8.45 (8.40—8.54)	8.5; 8.6; 8.3; 8.4; 8.3
NBS 55b	Ingot iron	1 g	0.006 (0.005—0.008)	0.0045; 0.0045
NBS 160	19Cr-9Ni-3Mo steel	150 mg	0.059 (0.054—0.064)	0.075; 0.075; 0.075 (with nitroso-R-salt 0.075—0.080)
NBS 161	64Ni-17Cr-15Fe casting alloy	20 mg	0.47 (0.45—0.49)	0.49; 0.49
NBS 162	66Ni-29Cu alloy	8 mg	0.54 (0.53—0.55)	0.53; 0.54
BCS 220	W-Mo high speed steel (6.7 % W; 4.2 % Mo; 1.3 % V)	6 mg	0.67 (0.64—0.68)	0.67; 0.67
BCS 233	Permanent Magnet Alloy (11 % Ni; 7 % Al; 5 % Cu; 0.8 % Ti)	0.3; 0.8 mg	23.72 (23.53—23.92)	23.8; 23.6; 23.8

SUMMARY

An improved procedure has been described for the photometric determination of cobalt by extraction of the β-nitroso-α-naphthol complex with chloroform. This procedure can be applied in the presence of large amounts of foreign elements. Interfering elements are: gold, palladium, platinum and copper (above 25 mg).

The method has been applied to the determination of cobalt in steels, non-ferrous alloys and nickel.

RÉSUMÉ

Les auteurs ont amélioré la méthode de dosage photométrique du cobalt par extraction au chloroforme de son complexe avec le β-nitroso-α-naphtol. Cette détermination peut être effectuée en présence de fortes teneurs en éléments étrangers. Les éléments gênants sont: or, palladium, platine et cuivre (> 25 mg). Cette méthode a été appliquée au dosage du cobalt dans les aciers, les métaux non ferreux et le nickel.

ZUSAMMENFASSUNG

Es wird ein verbessertes Verfahren beschrieben für die photometrische Bestimmung des Kobalts durch Extraktion des β-Nitroso-α-Naphthol-Komplexes mit Chloroform. Das Verfahren kann in Anwesenheit erheblicher Mengen fremder Elemente ausgeführt werden. Störende Elemente sind: Gold, Palladium, Platin und Kupfer (über 25 mg).

Es werden Anwendungen gegeben für die Bestimmung des Kobalts in Stahl, Nichteisenlegierungen und Nickel.

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URANYL OXINATES
A SPECTROPHOTOMETRIC STUDY

by

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In a previous communication[1] a study of the oxinates of thorium was reported in which the individuality of the 4- and 5-oxinates was definitely established. Besides thorium, uranium (UO_2^{+2}), scandium and plutonium give, in addition to the normal compounds, complexes with an additional oxine molecule. Here the uranyl 3- and 2-oxinates are reported; the former is orange red and is formed in aqueous solution, the latter is prepared by the heating of the former at 200° C and is olive-green in appearance[2]. The uranyl-3-complex has been assumed, by analogy with the thorium complex, to be a molecular compound of the 2-complex and oxine. There are however marked differences in the behaviour of thorium and uranyl complexes. In the first instance while either the 4- or the 5-complex of thorium may be precipitated from solution by choosing proper conditions, uranium separates only as the trioxinate and the dioxinate may be obtained only by the thermal decomposition of the former under controlled temperature conditions. Secondly, the oxinates of thorium are fairly stable in aqueous solution in the presence of excess reagent, but uranyl dioxinate is rapidly converted to the trioxinate on contact with a solution of the reagent. This behaviour of the uranium complexes suggests that the trioxinate is probably an interstitial compound. Spectro-chemical data on uranyl oxinates were however lacking. From such studies it has now been shown that the third molecule of oxine is bound by other than interstitial forces, since these are too weak to persist in solutions of polar solvents such as acetone. The absorption spectra of the two complexes in acetone *n*-amyl alcohol, *iso*butyl alcohol, and chloroform have been studied and it has been shown that the binding in the 2-oxinate appears to differ from that in the 3-oxinate.

The precipitation of oxinates of metals depends largely on pH[3]; while some, Zr, Th, *etc.* separate from acid solution, others, such as Be, are formed in a solution of high pH. Structurally, as judged from absorption spectra, two types of oxinates seem to exist; in one class the absorption of the reagent is intensified, while in the other bathochromic shifts of absorption peaks occur. Zr, Th, Be *etc.*, belong to the first class and Al, Ga, and other group III B elements[4] to the latter. This division according to chromic behaviour bears no relation to the pH of precipitation. A factor complicating the study of the structures of the complexes from absorption studies is the change in absorption spectra which oxine exhibits with pH. These changes however do not, in most cases, appear in the absorption of the metal complex. The two types of metal complexes have thus to be distinguished by the type of bond that oxine forms with the metallic ion and the nature of this bond is possibly connected with the electronic structure of the binding atom.

EXPERIMENTAL

Reagents: — (1) Uranyl solution: — A stock solution of pure uranyl nitrate was prepared as described in a previous paper[2]. It was suitably diluted, when required, to give a solution $0.9995 \cdot 10^{-3} M$ in doubly distilled water.

(2) Oxine solution: — A similar solution, which could be conveniently diluted to $0.9995 \cdot 10^{-3} M$ was prepared by dissolving an accurately weighed quantity of AnalaR oxine in $2.5 N$ acetic acid.

(3) pH adjustments were made by adding the requisite amounts of freshly distilled and diluted ammonia or dilute acetic acid. A bench type Cambridge pH meter with a glass electrode was used for the pH measurements.

Absorption measurements were made with a Beckman D.U. model spectrophotometer in 1 cm matched silica or Corning glass cuvettes. A hot filament tungsten lamp provided from 600 to 350 mμ, and a hot cathode hydrogen lamp was used below this region. The slit was the narrowest possible consistent with the balance of the instrument, in order to maintain a good degree of spectral purity.

The formation of the uranyl complex was first studied for its dependence upon pH. The corresponding changes in absorption by the reagent were also studied. Making the assumption (*vide infra*) that the stoichiometric ratio of uranyl ions to oxine molecules is 1 : 3 the uranium and reagent solutions were mixed in the requisite proportions and their optical densities were determined. The results are shown in Fig. 1a and 1b.

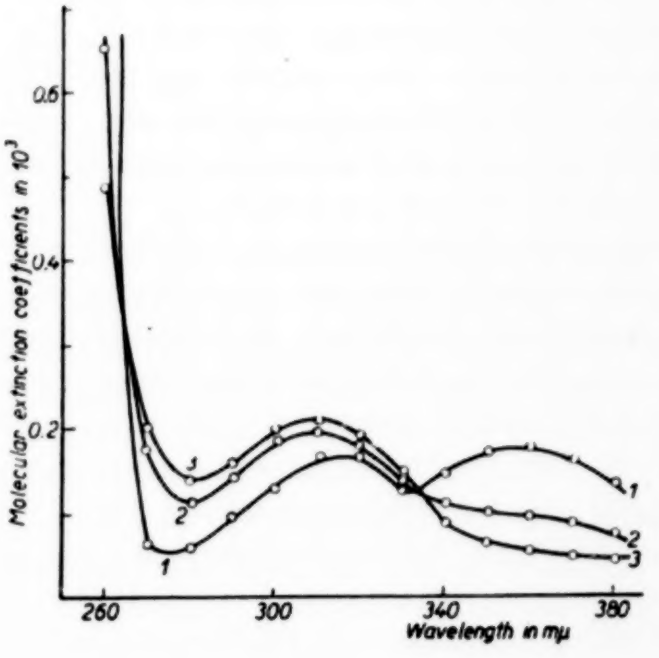

Fig. 1a. 1 pH = 3.48
2 pH = 5.26
3 pH = 5.59

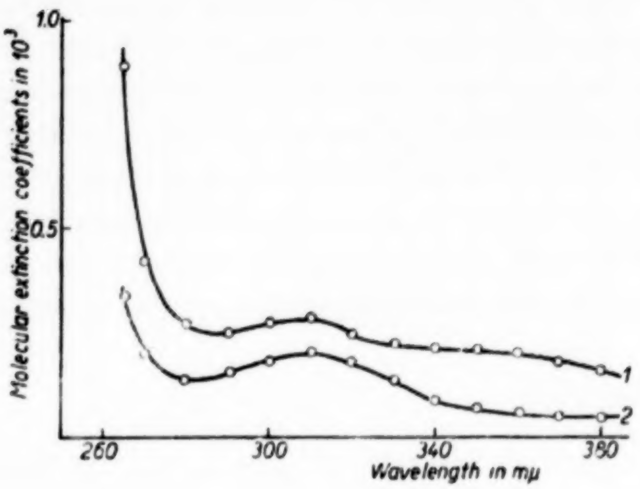

Fig. 1b. 1 Complex
2 Reagent

From the curves of Fig. 1a it is evident that oxine exists in two forms in acid and neutral solutions with isobestic points at 332 and 265 mμ respectively. In addition there is one at 245 mμ which is not shown. EWING AND STECK[6] mention that a further change in the absorption occurs in strongly alkaline solution, pH 12 (*vide infra*). In acid solution three absorption peaks are present at 360, 320 and 250, mμ respectively. On passing into neutral solution the one at 360 mμ disappears reappearing in a spread-band form at pH 12 (*cf.* EWING AND STECK) while those at 320 and 250 mμ shift to 310 and 240 mμ respectively. The isobestic point at 332 mμ appears to possess a special interest and significance; it may be considered as the point at which the oxine molecule changes from the neutral to the acid form. When the pH decreases, a general decrease in the absorption occurs below this wavelength, while above this point absorption increases, thus showing an increase in the acidic form and a consequent decrease in the neutral form. During complex formation the neutral form appears to be stabilized.

Uranyl-3-oxinate

Absorption measurements on the complex show that complex-formation is virtually absent below a pH of 3.5; at pH 4.27 complex formation is in evidence and there is no further increase in optical density above pH 5.3; consequently all measurements were carried out at pH 5.25. In Fig. 1b are shown the absorption curves for the reagent and the complex in this pH range.

Preliminary determinations of the complex formed indicated that even under differing conditions of reagent concentration and temperature only uranyl trioxinate separated and the effect of the addition of an insufficient quantity of the reagent resulted in incomplete precipitation of uranyl ions.

Evidence for the stoichiometric composition of the complex in solution was

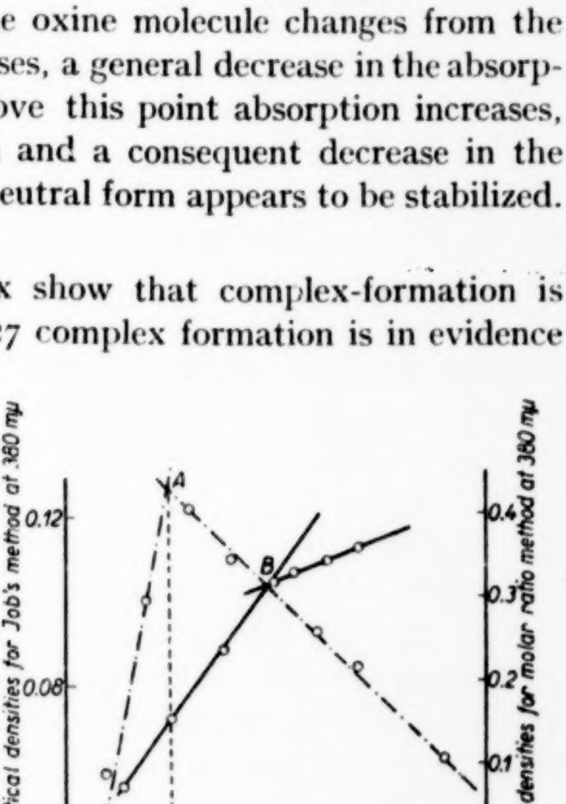

Fig. 2. A Job's method
B Molar ratio method

obtained in two ways, by Job's method of continuous variations (Fig. 2) and by the molar ratio method (Fig. 2B). Both procedures indicated a 1 : 3 ratio of uranyl to oxine. A slight variation of the latter procedure yielded interesting results concerning the stability of the complex. Varying volumes of an equimolar oxine solution were added at pH 5.25 to a fixed volume of uranyl solution (10 ml) at the same pH and in order to bring the optical density within reasonable limits, the mixture was diluted to 100 ml with water of identical pH. Absorption measurements were made at 3 different wavelengths lying on either side of the acid-neutral isobestic point at 332 mμ. The results are shown in Table 1.

TABLE I

FORMATION AND STABILITY OF URANYL-3-OXINATE

pH 5.25 Total volume 100 ml
Conc. of uranyl solution: $0.9995 \cdot 10^{-3} M$
Conc. of oxine solution: $0.9995 \cdot 10^{-3} M$
Volume of uranyl solution: 10 ml

Volume of oxine added in ml	Optical densities of the mixture at 380 mμ	320 mμ	290 mμ
10	0.149	0.245	0.252
20	0.288	0.489	0.503
30	0.450	0.719	0.760
40 (a)	0.500	0.896	0.904
oxine alone 10 (b)	0.043	0.184	0.154
(a-b)	0.457	0.712	0.749

Thus when progressive amounts of oxine are added to a uranyl solution, the optical density of the resulting mixture correspondingly increases until the stoichiometric ratio 1 : 3 of uranyl to oxine is reached. Further addition of the reagent does not lead to an increase of the amount of oxine in the complex, the increase in the optical density of the mixture being fully accounted for by the optical density of the excess reagent. This leads to the conclusion that the reaction

$$UO_2^{+2} + 3OX \rightleftharpoons UO_2\,(OX)_3$$

proceeds almost completely to the right. The same is indicated by the sharp bend in curve B of Fig. 2 (molar ratio method) and by the sharp peak in the curve obtained by Job's method.

Since the 2-oxinate of uranium is not soluble in water, a comparative study of the absorption of the two complexes is possible only in non-aqueous solvents. Both complexes dissolve readily in chloroform, *iso*butyl alcohol, *n*-amyl alcohol, acetone and a number of other organic solvents, but they are not soluble in benzene. The present study has been confined to the solvents mentioned above. Absorption in conformity with Beer's law is an essential prerequisite to a comparison of extinction coefficients. While oxine obeys Beer's law to a considerable extent in all these solvents, the di- and trioxinates deviate appreciably in some aspects. However, data obtained under comparable conditions are of some value in a study of the characteristics of the complexes. The range of validity, both in concentration and wavelength, is given for each of the solvents in Table II.

In addition to those noted above, other spectral regions of approximate validity may be utilized for comparison without producing a large degree of uncertainty as to the validity of the conclusions. These ranges have been selected and in Table III some useful data are presented. Besides the molar extinction coefficients of the reagent and the di- and tri-oxinates, other derived quantities are shown, which throw light on the characteristics of the complexes. What may be termed the fractional intensification (designated by + sign) or reduction (— sign) of the molar extinction coefficient per oxine ligand in the complex is shown. This fraction was obtained as follows. The extinction coefficient due to two or three molecules of oxine (as the case may be) was substracted from the molar extinction coefficient of the complex and the difference, divided by the subtractant, yielded the figures noted. These figures give the effect of complex formation or bond formation on the absorption of oxine.

TABLE II

RANGE OF VALIDITY OF BEER'S LAW

Solvent	2 complex Conc. in mg per ml	 Wavelength mμ	3 complex Conc. in mg per ml	 Wavelength mμ
Aceton	up to 0.08	below 400	0.08	below 400
Chloroform	up to 0.06	300-290	0.06	330-290
*Iso*butyl alcohol	up to 0.06	below 380	0.06	below 380
n-Amyl alcohol	up to 0.07	—	—	—

A study of Table III reveals that at practically all wavelengths and in all solvents the sum of the extinction coefficients for one molecule each of oxine and the 2-complex does not equal the extinction coefficient of the 3-complex — it is higher in some regions and lower in others. In a general way this sum is higher in the region of absorption of the reagent and lower in the other regions. An interesting fact is that although the complex (2- or 3- oxinate) gives apparently a higher molar extinction coefficient than the reagent, the effect of complex formation actually appears to be a reduction in the intensity of the absorption of the reagent in the neighbourhood of the peak. In regions where the reagent does not absorb or absorbs only faintly, complex formation leads to intense absorption. The absorption peak of the reagent varies with the nature of the solvent. Thus a peak occurring at 310 mμ in water and chloroform shifts to 320 mμ in *iso*butyl alcohol and to 330 mμ in acetone and *n*-amyl alcohol. Because of the strong absorption due to the solvent alone, the absorption could not be studied at wavelengths shorter than those listed in the table.

The fractional deviations (columns 4 and 6 of Table III) though differing in

TABLE III

Solvent : Chloroform.

Wave length	$E \times 10^3$ Reagent	E of 2-Complex	Fractional deviation in E	E of 3-complex	Fractional deviation in E
350	0.75	2.41	+0.45	4.79	+0.85
340	1.57	3.36	+0.11	5.06	+0.11
330	2.33	4.41	—0.12	5.71	—0.43
320	2.73	4.91	—0.28	5.79	—0.80
310	2.83	5.02	—0.22	5.91	—0.86
300	2.60	4.23	—0.48	5.76	—0.71
290	2.08	3.64	—0.26	5.43	—0.27
280	1.86	4.82	+0.55	14.03	+2.82
270	2.12	11.19	+3.5		
					Very high +
Solvent: *iso*-Butyl alcohol.					
400	—	2.72	—	2.88	—
380	0.21	3.51	+7.3	4.10	+6.0
360	0.34	3.66	+4.3	4.21	+3.5
350	0.72	3.74	+1.6	4.32	+1.0
340	1.43	3.81	+0.33	5.51	+0.3
330	2.18	4.58	+0.05	6.02	—0.08
320	2.63	4.71	—0.10	6.71	—0.15
310	2.53	4.63	—0.08	6.62	—0.12
300	2.10	4.26	—	5.81	—0.08
Solvent: Acetone					
400	0.04	3.92	+48	4.39	+35.5
390	0.04	4.78	+59	5.13	+41.7
380	0.04	5.14	+63	5.38	+44.7
370	0.05	5.10	+50	5.28	+34.2
360	0.14	4.69	+15.8	4.79	+10.0
350	0.51	4.24	+3.16	4.42	+1.9
340	1.51	4.40	+0.46	4.78	+0.05
330	2.06	4.63	+0.38	5.50	—0.12
325	2.02	4.76	+0.18	5.63	—0.07
Solvent: *n*-Amyl alcohol					
350	0.63	3.91	+2.0	4.49	+1.30
340	1.36	4.15	+0.55	5.49	+0.40
330	2.15	4.52	+0.05	6.48	—
320	2.08	4.42	+0.06	6.18	—

magnitude, follow practically the same order in both the 2- and 3-complexes. They reach the highest negative values at the peak of absorption of the reagent in the solvents. An exception however occurs in chloroform with the 2-complex, when this shifts to a slightly lower wavelength, 300 mμ instead of 310 mμ. These considerations characterize the uranyl 2- and 3-complexes as different species.

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THE STRUCTURE OF OXINE

The structure of oxine in acid, neutral and alkaline solutions is a debated matter. STONE AND FRIEDMAN[7] pictured an intra-molecular change, a ketonic group developing on transition from neutral to acid or from neutral to alkaline medium. MOELLER AND PUNDSACK[8] disagree with this view and postulate hydrogen bond formation in acid solution. Oxine shows different structures (a) in acid, below pH 4.0 (b) neutral pH 4 to 10 and (c) alkaline, pH 12, solutions. There are three band systems in alkaline or acid mediums and only two in neutral solution as indicated below.

		System 240-250 mμ	System 310-320 mμ	System 360 mμ
(1)	Neutral pH 4-10	Very intense at 240.	Intense at 310	Does not exist
(2)	Acid pH 4.0	Shifts to 250 Intensity very nearly the same as in neutral solution.	Shifts to 320 Intensity considerably less; about 2/3 of the one in neutral solution.	Appears at 360 Intensity about the same as at 310-320.
(3)	Alkaline pH 12	Shifts to 250 slightly less intense.	Spread band from 325-355 equally intense as 310 band in neutral solution.	

The peak of absorption at 240 mμ in the neutral molecule maintains its character both in acid and alkaline media and only suffers a shift to 250 mμ, a mere loading effect. The peak at 310 mμ appears to belong to a different part of the molecule, undergoing different changes in acid and alkaline solutions. In acid solution there is both a bathochromic shift and the development of a new absorption peak. The intensities of the two maxima are about the same. In alkaline solution the band at 310 mμ spreads into a broad band from 325-360 mμ. In this connection the observation (EWING AND STECK) that the methyl ether shows no change in absorption from neutral to alkaline solution and its absorption is almost identical with that of the parent substance-oxine is of interest. In acid solution the band at 360 mμ is produced both in oxine and the ether with the same intensity. The 240-250 mμ band appears to be characteristic of naphthols (EWING AND STECK) and the 310-320 mμ band of pyridine (STONE AND FRIEDMAN). The naphthol peak is not altered in acid solutions, only slight bathochromic shifts arise. On the other hand the 310-320 mμ band characteristic of pyridine undergoes radical changes in acid as well as alkaline media. MOELLER AND PUNDSACK's assumption that a hydrogen bond is formed in acid solution does not seem justifiable since ether in which such binding is precluded has a practically identical spectrum. From the evidence available concerning the absorptions of oxine and its methyl ether, in acid, neutral and alkaline solutions, it appears probable that in acid solution the oxine molecule takes up a proton of the acid to assume the structure (I),

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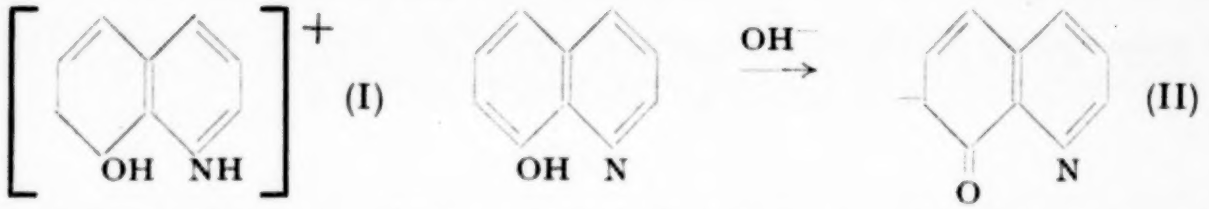
and in alkaline solution an intramolecular change as envisaged by Stone and Friedman occurs to give (II),



and the resonant forms which are not indicated for considerations of space.

The structure of uranyl oxinates. Changes in absorption spectrum from that of the component ion are indicative of the formation of covalent bonds and qualitatively the more marked the change, the more covalent is the bond. The high percentage of intensification or reduction observed in certain spectral regions on complex formation in oxine (large positive or negative values in columns 4 and 6 of Table III) shows the formation of a bond with a high degree of covalency. On the other hand the insolubility of the complex in nonpolar solvents such as benzene and carbon tetrachloride points to an intrinsic ionic character. This intrinsic ionic character is also supported by the interesting observation that uranyl oxinate couples with diazotized sulphanilic acid to give an intensely coloured complex. Thus one should postulate a mixed bond with a high degree of covalence.

SUMMARY

From spectrophotometric studies of the 2- and 3-oxinates of uranyl in various non-aqueous solvents it has been shown that the two complexes possess different structures. The change in absorption of oxine in acidic and alkaline solutions has been explained.

RÉSUMÉ

Après une étude spectrophotométrique des 2- et 3-oxinates d'uranyle, dans différents solvants non aqueux, il a été démontré que ces deux complexes présentent diverses structures. On a pu expliquer le changement d'absorption de l'oxine en solutions acides et alcalines.

ZUSAMMENFASSUNG

Es wurde gezeigt nach spektrophotometrischen Untersuchungen der 2- und 3-Oxinate des Uranyls, dass in verschiedenen nicht-wässrigen Lösungsmitteln, die beiden Komplexe verschiedene Strukturen besitzen. Die Änderung in der Oxinabsorption in sauren und alkalichen Lösungen wurde auch erklärt.

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THE HETEROMETRIC MICRODETERMINATION OF MERCURY OR MERCAPTOBENZTHIAZOLE

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INTRODUCTION

The heterometric behaviour of mercury towards mercaptobenzthiazole (=MBT) and the different complex compounds which are obtained, are dealt with in a special report[1]. In this paper we deal with the analytical aspect of the reaction.

The heterometric determination of mercury by MBT or, *vice versa*, the determination of MBT with mercuric nitrate are very sensitive reactions. 2 mg Hg in 20-30 ml (concentration: $5 \cdot 10^{-4} M$) or 1-2 mg MBT in 20-30 ml solution can be determined easily and the error amounts to 0-3%. The titration time is 15-30 minutes. There are different working possibilities. This method is especially suitable for the determination of mercury in the presence of other metals (see next report). An aqueous, as well as an alcoholic solution ($\leqslant$ 50% alcohol) may be used for the analysis, which may be carried out with the same sensitivity in the pH-region of ∼2 pH — 10 pH. In the case of MBT-determination, two analytical end-points are obtained in each titration and the first point (the point of the initial precipitation) gives a rough orientation about the expected more precise second end-point, which coincides with the first optical maximum density point. The mercury on the other hand can be determined either in an alkaline or in an acidic $\leqslant$ 50% alcoholic solution; in the former case a maximum density *point* is obtained and then the density drops, while if titrated in acidic solution a maximum density *line* is obtained instead. This different behaviour is caused by the fact that $Hg(MBT)_2$ is soluble in the alkaline solution giving the anion complex $[Hg(MBT)_4]^{-2}$. The influence of citrate, tartrate, ethylenediaminetetraacetate and KCN was studied. These solutions were later used by us for the determination of mercury in the presence of copper, bismuth, *etc.*

Under all circumstances the insoluble $Hg(MBT)_2$ is obtained and the amount present determined. As this compound is soluble in solutions containing a higher percentage of alcohol, the content of alcohol must be restricted to $\leqslant$ 50%. A 25% alcohol is in many cases already sufficient to obtain a reproducible maximum density. If the alcohol content is insufficient a precipitate floats on the surface, the density values show fluctuations and the determination of the end-point becomes uncertain.

A selection of experiments which were carried out and the results obtained, are compiled in Tables I-III. The course of some heterometric titrations is shown in the diagram (the experiment number and the curve number correspond to facilitate comparison).

EXPERIMENTAL

The same apparatus and the same technique were used as in previous investigations[2]. The MBT was a BDH reagent and the $Hg(NO_3)_2$ was a May & Baker, crystals, reagent.

On dissolving the mercuric nitrate in water, a slight turbidity was observed. By the addition of a minimum number of drops of nitric acid, the solution became clear and further dilution could be carried out without difficulty. The alcohol used was redistilled alcohol of approximately 95%. All the other chemicals were analytical reagents or chemically pure reagents. All titrations were made at 20° C.

RESULTS AND DISCUSSION

1. *Determination of mercury*

(a) *Influence of pH and medium*

Parallel pH and heterometric titrations were carried out with a mixture of mercuric nitrate and a 2-3 fold molar excess of MBT, in order to study the solubility of mercuric MBT at different pH's. The density values obtained were independent of the pH of the solution in the region of ∼1 pH — 10 pH. Table I (Fig. 1) gives the composition and results of a series of experiments which were carried out with the purpose of studying the conditions necessary for a quantitative determination of mercury with MBT. If we compare experiments 1, 2, 5 and 6, we see that the presence of a strong acid in large amounts reduces the maximum density

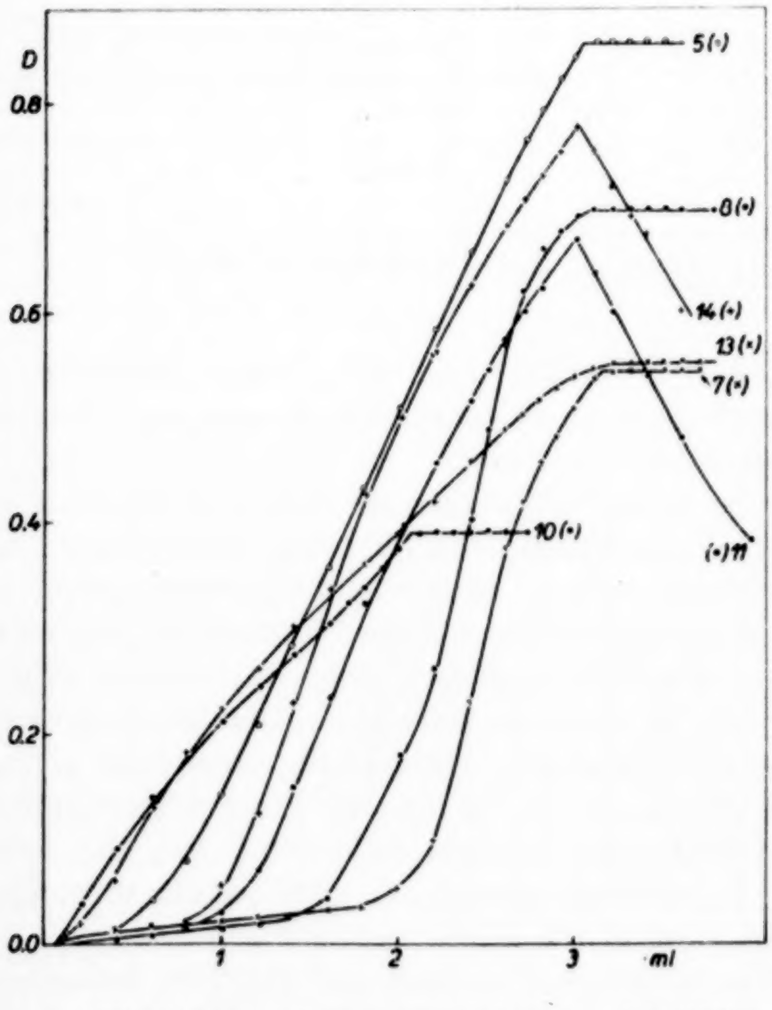

Fig. 1. Titrations of mercuric nitrate with MBT in aqueous or alcoholic solutions at different pH's.

TABLE I

Composition: 5 ml 0.002M $Hg(NO_3)_2$ + 15 ml Complements + x ml nM Mercaptobenzthiazole (alc.) (= MBT)

Ex-pt. No.	pH of the solution	MBT		Components
		x ml	molarity	
1	∿1	2.95	0.0066	1 ml 0.1N HNO_3 + 14 ml H_2O
2	<1	∿2.8	0.0066	5 ,, 0.1 ,, ,, + 10 ,, ,,
3	∿1	3.00	0.0066	1 ,, 0.1 ,, ,, + 4 ,, ,, + 10 ml alc.
4	∿3.0	2.03	0.01	1 ,, N CH_3COOH + 14 ml H_2O
5	∿3	3.04	0.0066	1 ,, ,, ,, + 14 ,, ,,
6	∿3	3.1	0.0066	3 ,, ,, ,, + 12 ,, ,,
7	∿3	3.08	0.0066	1 ,, ,, ,, + 4 ,, ,, + 10 ml alc.
8	∿3	3.1	0.0066	3 ,, ,, ,, + 2 ,, ,, + 10 ,, ,,
9	∿7	3.17	0.0066	1 ,, N CH_3COONa + 14 ml H_2O
10	∿7	2.12	0.01	1 ,, ,, ,, + 14 ,, ,,
11	∿7	3.00	0.0066	1 ,, ,, ,, + 4 ,, ,, + 10 ml alc.
12	∿7	2.08	0.01	1 ,, ,, ,, + 4 ,, ,, + 10 ,, ,,
13	∿8.5	3.20	0.0066	1 ,, 2N NH_4NO_3 + 2 ml 0.1N NaOH + 12 ml H_2O
14	∿8.5	3.00	0.0066	1 ,, ,, ,, + 2 ,, ,, ,, + 2 ,, ,, + 10 ,, alc.
15	∿8.5	2.06	0.01	1 ,, ,, ,, + 2 ,, ,, ,, + 2 ,, H_2O + 10 ,, alc.
16	∿8.5	1.03	0.02	1 ,, ,, ,, + 2 ,, ,, ,, + 2 ,, H_2O + 10 ,, alc.
17	∿8.5		0.02 (2 ml)	1 ,, ,, ,, + 2 ,, ,, ,, + 15 ,, ,,

† — means no change of density occurs on further addition of MBT
* = result uncertain.

value and makes the end-point uncertain (exp. 2). Larger amounts of acetic acid cause the precipitate to float on the surface and cause disturbances and errors in the determination of the end-point.

In alcoholic solution (exp. 8) no such disturbances are observed. Working in alkaline solution (pH's > 7-10) we established the following facts. Use of an aqueous solution causes disturbances and the results are uncertain (exps. 9, 10, 13). Therefore, a ⩽ 50% alcoholic solution must be used instead. No precipitation occurs if the alcohol content is greater than 50% (exp. 17) because of the solubility of $Hg(MBT)_2$ in alcohol. In alcoholic solutions a maximum density *point* is obtained and the excess MBT gradually dissolves the precipitate giving the anion complex $[Hg(MBT)_4]^{-2}$ (exps. 11, 12, 14-16). The exact determination of the maximum density point sometimes involves difficulties, and the cases where a maximum density *line* is obtained instead are more satisfactory. The danger of a dissolution does not exist in the *acidic* alcoholic solution (exp. 8). In the latter case, a density *line* is obtained instead and the first maximum density point is obtained by the intersection of the two lines (the line of the last part of the titration with the horizontal maximum density line).

Content: 2.006 mg Temp. = 20° C

Remarks	Titration time in min	Initial precip. at ml	Max. density value	% Error
	40	0.4	0.69 †	—1.7
Part of the suspension floats on the surface	25	0.8	0.50	
Maxim. point, then the density drops	26	1.0	0.79	0.0
	23	0.0	0.81	+1.5
	22	0.2	0.86	+1.3
Part of the precipitate floats on the surface	23	0.2	0.91	+3.3
	15	0.4	0.55	+2.7
	24	0.4	0.70	+3.3
A suspension on the surface	15	0.2	0.59	
,, ,, ,, ,, ,,	12	0.0	0.39	
After the maximum point slowly dissolves	25	0.4	0.67	0.0
,, ,, ,, ,, ,, ,,	23	0.6	0.67	+4.0
A suspension on the surface	12	0.0	0.55	
After the maximum point slowly dissolves	26	0.6	0.78	0.0
,, ,, ,, ,, ,, ,,	26	0.4	0.69	+3.0
,, ,, ,, ,, ,, ,,	18	0.0	0.68	+3.0

precipitation

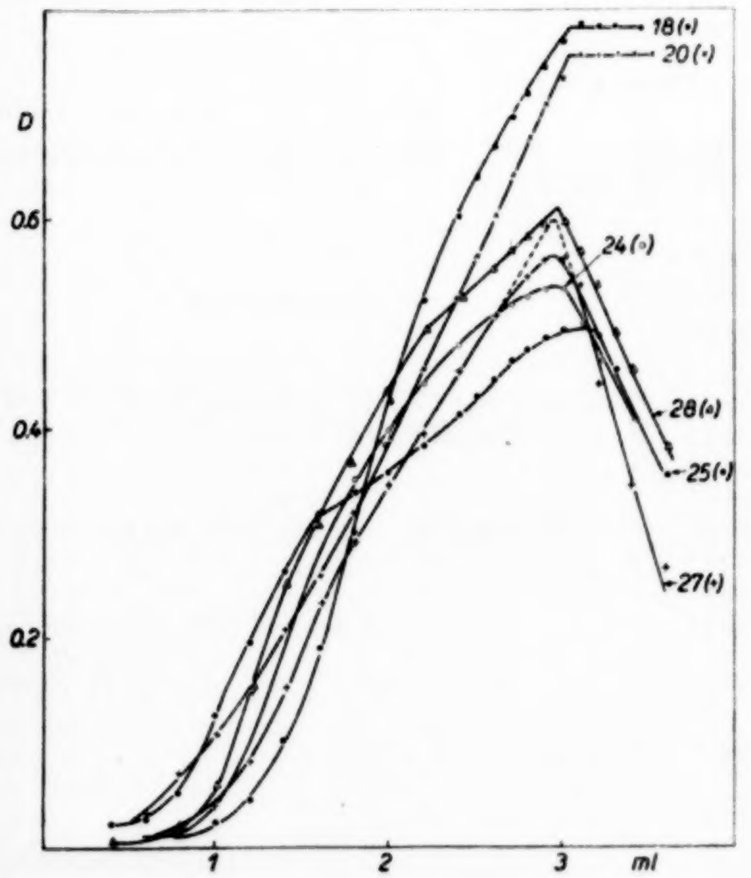

Fig. 2. Titrations of mercuric nitrate with MBT in the presence of different complexing agents.

(b) *Influence of complexing agents*

Table II (and Fig. 2) gives a selection of such experiments. They were all carried out with the purpose of using the results for further experiments (see the next report) on the determination of mercury in the presence of foreign metals. The composition of some experiments is even adaptable to cases where a foreign metal such as copper or bismuth is present in large excess. Solutions of trisodium-

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TABLE II

Composition: 5 ml 0.02*M* $Hg(NO_3)_2$ + 15 ml complements + x ml n*M* mercaptobenzthiazole (alc.) (= MBT)

Expt. No.	pH of the solution	MBT x ml	MBT molarity	Components
18	∿7.0	3.04	0.0066	2 ,, *N* CH_3COONa + 2 ml 0.1*M* EDTA-Na_4 + 11 ml H_2O
19	∿3.0	30.4	0.0066	1 ,, ,, ,, + 2 ,, ,, ,, + 12 ,, ,,
20	∿3.0	3.03	0.0066	3 ,, ,, CH_3COOH + 2 ,, ,, ,, + 10 ,, ,,
21	∿7.0		0.01	1 ,, ,, CH_3COONa + 2 ,, 0.05*M* ,, + 2 ,, H_2O + 10 ml alc.
22	∿8.5		0.01	1 ,, 2*N* NH_4NO_3 + 2 ml 0.1*N* NaOH + 2 ml 0.05*M* EDTA-Na_4 + 10 ml alc.
23	∿7.0	∿3.1	0.0066	2 ,, *N* CH_3COONa + 2 ml *M* Na_3-citrate + 11 ml H_2O
24	∿7.0	2.95	0.0066	2 ,, *N* ,, + 2 ,, ,, ,, + 1 ml H_2O + 10 ,, alc.
25	∿9.5	3.1	0.0066	1 ,, 2*N* NH_4HO_3 + 2 ml *N* NH_3 + 2 ml *M* Na_3-citrate + 10 ,, alc.
26	∿7.0	∿3.2	0.0066	2 ,, *N* Na-acetate + 2 ml *M* Na_2-tartrate + 11 ,, H_2O
27	∿7.0	2.95	0.0066	2 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, H_2O + 10 ,, alc.
28	∿9.5	3.04	0.0066	1 ,, 2*N* NH_4NO_3 + 2 ml *N* NH_3 + 2 ml *M* Na_2-tartrate + 10 ml alc.
29	∿7.0		0.01	1 ,, 0.1*N* Na-acetate + 2 ml 0.1*N* KCN + 12 ml H_2O

† —— means no change of density occurs on further addition of MBT
* = result uncertain.

TABLE III

Composition: 5 ml m*M* mercaptobenzthiazole (= MBT) (alc.) + (20-a) ml complements + x ml n*M* $Hg(NO_3)_2$

Expt. No.	pH of the solution	$Hg(NO_3)_2$ x ml	$Hg(NO_3)_2$ molarity	MBT molarity	Components
30	∿3.0	∿2.3	0.0033	0.0033	3 ml *M* CH_3COOH + 12 ml H_2O
31	∿7.0	2.48	0.0033	0.0033	1 ,, ,, CH_3COONa + 14 ,, ,,
32		2.49	0.002	0.002	1 ,, ,, ,, + 14 ,, ,,
33		2.47	0.001	0.001	1 ,, ,, ,, + 14 ,, ,,
34	∿8.5	2.47	0.0033	0.0033	2 ,, *N* NH_4NO_3 + 2 ml 0.1*N* NaOH + 11 ml H_2O
35		2.47	0.002	0.002	2 ,, ,, ,, + 2 ,, ,, ,, + 11 ,, ,,
36		2.47	0.001	0.001	2 ,, ,, ,, + 2 ,, ,, ,, + 11 ,, ,,
37	∿9.5	2.48	0.0033	0.0033	2 ,, ,, ,, + 2 ,, *N* NH_3 + 11 ml H_2O (vol. = 30 ml)
38		2.47	0.002	0.002	2 ,, ,, ,, + 2 ,, ,, + 11 ml H_2O (vol. = 30 ml)
39		2.44	0.001	0.001	2 ,, ,, ,, + 2 ,, ,, ,, + 11 ml H_2O (vol. = 30 ml)

Temp. = 20° C Content: 2.006 mg Hg

Remarks	Titration time in min	Initial precip. at ml	Maxim. density value	% Error
	19	1.0	0.78†	+1.3
	45	0.4	0.76	+1.3
	32	0.5	0.76	+1.0
	10	∞	0.0	
	5	∞	0.0	
* Fluctuations, suspension on the surface	15	0.0	0.52	+3.3
Excess dissolves gradually	22	0.6	0.53	—1.7
,, ,, ,,	17	0.2	0.50	+3.3
* A precipitate on the surface; maximum, then drop	12	0.0	0.70	
Excess dissolves gradually	26	0.4	0.56	—1.7
,, ,, ,,	18	0.7	0.59	+1.3
No precipitate	6	∞	0.0	

MBT contents: 0.836 mg
1.672 ,,
2.7588 ,,

Temp. = 20° C

	Titration time in min	Initial precip. at ml	Maxim. density value	Error		
				%	γ	γ/ml
Precipitate floats on the surface	13	0.0	0.63			
After the maximum, density drops	7	0.0	0.91	—0.8	22.1	1.1
,, ,, ,, ,, ,,	14	0.4	0.87	—0.4	6.7	0.3
,, ,, ,, ,, ,,	25	0.4	0.35	—1.2	10.1	0.5
,, ,, ,, ,, ,,	19	0.0	1.02	—1.2	33.1	1,7
,, ,, ,, ,, ,,	15	0.0	0.80	—1.2	20.2	1.0
,, ,, ,, ,, ,,	20	0.4	0.47	—1.2	10.1	0.5
,, ,, ,, ,, ,,	20	0.0	1.00	—0.8	22.1	0.7
,, ,, ,, ,, ,,	12	0.0	0.77	—1.2	20.2	0.7
,, ,, ,, ,, ,,	23	0.4	0.51	—2.4	20.2	0.7

citrate, disodiumtartrate, KCN and ethylenediaminetetraacetate (= Na_4-EDTA) were prepared and their influence on the precipitation of mercury under different working conditions, was studied.

Ethylenediaminetetraacetate. The experiments were chosen for their use in the determination of mercury in the presence of metals as copper or bismuth. Experiments 18-22 give the results with EDTA-Na_4. As can be seen *alcoholic* solutions cannot be used when the titration is carried out in the presence of sodium acetate or at higher alkalinity. No precipitation of mercury occurs; this may be due to the stabilization of the Hg-EDTA complex in the presence of alcohol. In *aqueous* solution (contrary to experiments 6 and 9, Table I) we were able to titrate without disturbances, either in acetate (exp. 1) or in acetic acid solutions (exps. 2 and 3).

Trisodiumcitrate. From previous investigations[3] we know that many metals form very strong bonds with the citrate or tartrate anions, especially in alkaline solution. The experiments were therefore carried out in alkaline solutions. Here too, the results were uncertain when aqueous solutions were used (exps. 23, 26), and therefore alcoholic solutions were used instead. Although the maximum density values seem somewhat depressed (exps. 24, 25), the determination could be carried out. From further experiments with citrate (see following report), we learned that there is practically no limit to the amount of trisodium citrate which may be present. This of course depends on the solubility of citrate in the alcoholic solution.

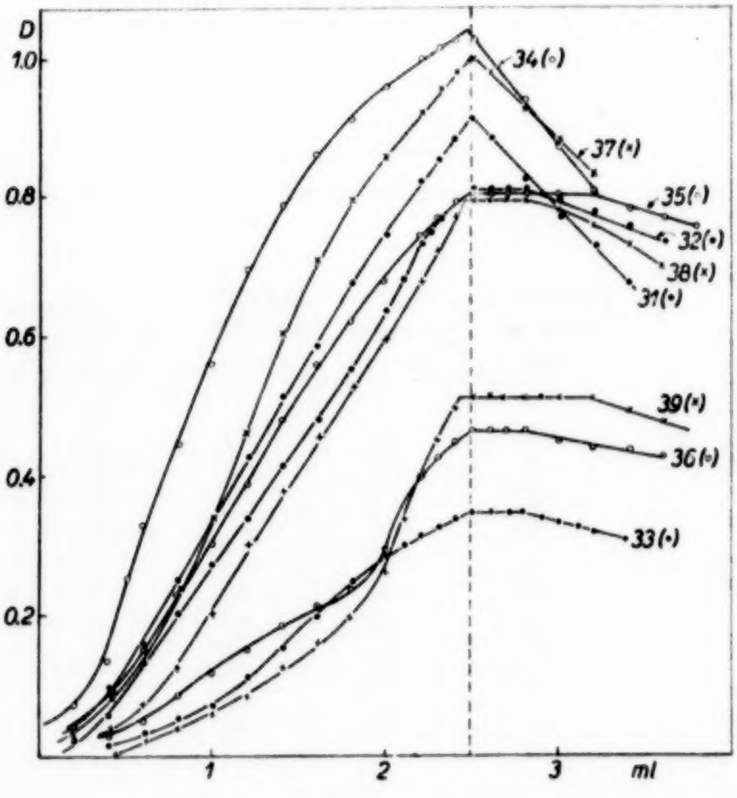

Fig. 3. Titrations of MBT in alkaline solutions with mercuric nitrate.

Disodiumtartrate. Analogous results were obtained as in the presence of citrate (exps. 26-28).

KCN. KCN dissolves the $Hg(MBT)_2$ in neutral or alkaline solutions (exp. 29) and cannot be present.

2. *The determination of mercaptobenzthiazole*

Table 3 (Fig. 3) presents a selection of experiments made for the purpose of studying the possibility of determining MBT by heterometric titration with a standardized aqueous solution of $Hg(NO_3)_2$. All the solutions contained 20-25%

alcohol at the beginning. As can be seen, this amount is sufficient to carry out titrations with mercury without any disturbances whatsoever. Whereas 20 ml solution was generally used, in the last three experiments the titrated volume was 30 ml. In the presence of 3 ml *M* acetic acid (exp. 1) this amount of alcohol is probably insufficient and the result is uncertain. In contrast to this, a 25% alcoholic solution is entirely sufficient to carry out titrations in acetate or stronger alkaline solutions. All the results are very satisfactory and the error was never higher than 2%. The titration time was also low. In most cases the maximum optical density remained constant, giving a short maximum density line, and then gradually dropped with the further addition of mercury. In the highest concentration of MBT (exps. 34, 37) a maximum point is obtained at the intersection of the two lines at a sharp angle. In all the other cases, the first maximum point is obtained from the intersection of the linear last portion of the titration curve with the horizontal maximum density line. The precision of the determination did not depend, in the alkaline solution, on the pH at which the titration was carried out.

Summarizing, we may say that 1-2 mg of MBT which is dissolved in 30 ml of a 20-25% alcoholic solution can be determined by the heterometric titration with mercury very satisfactorily. The titration time is about 10-20 minutes and the error is 0-2%.

METHOD

1. *Determination of mercury*

(a) *In acidic solution*: 20 ml of an aqueous solution of mercuric nitrate, which contains 1-2 mg mercury and 1 ml *M* acetic acid, are titrated heterometrically with an alcoholic solution of 0.01*M* — 0.005*M* mercaptobenzthiazole, using a microburet (0.01 ml). At the end of the titration a horizontal maximum optical density line is obtained. The location of the end-point is at the intersection of this line with the last part of the titration line.

Instead of an aqueous solution, a dilute alcoholic solution (∼ 25% alcohol) may be used. The titration time is about 30 min. Error 0-3%.

(b) *In alkaline solution*: 20 ml of a dilute alcoholic solution (25%-50%), which contains 1-2 mg mercuric nitrate, in addition to either 1 ml *M* sodium acetate or 1 ml 2*N* NH_4NO_3 together with 1 ml 0.2*N* NaOH, are titrated with an alcoholic solution of 0.01*M* — 0.005*M* mercaptobenzthiazole. At the theoretical end-point a sharp optical maximum density point is obtained (by the intersection of two lines). The titration time is ∼ 30 min. Error 0-3%.

Remarks: The acetic acid or acetate solutions may contain excesses of ethylenediaminetetraacetate, but in the more alkaline solution no precipitation occurs. Large excesses of sodium citrate or tartrate do not interfere at any pH. The alcoholic solutions of mercaptobenzthiazole are stable for many months if kept in darkness.

2. *The determination of mercaptobenzthiazole.*

The determination is carried out in acetate or in strong alkaline solution (pH = 8-9). 20-30 ml of a 20%-25% alcoholic solution, which contains 1-2 mg mercaptobenzthiazole, is titrated with an aqueous solution of 0.001*M* — 0.003*M* mercuric nitrate. The end-point of the titration (maximum optical density) is located at the intersection of the two lines.

The titrated solution may contain 1 ml *M* sodium acetate, or 1 ml 2*N* NH_4NO_3 together with 1 ml 0.2*N* NaOH (pH ∾ 8.5) or 1 ml 2*N* NH_4NO_3 together with 1 ml 2*N* NH_3 (pH ∾ 9.5). The titration time is 10-15 minutes. Error 1-2%.

SUMMARY

The heterometric determinations of mercury or mercaptobenzthiazole are very sensitive reactions. An aqueous or a dilute alcoholic solution is used and the titration may be carried out at pH 2-10. If mercaptobenzthiazole is determined, two analytical end-points are obtained: the first gives an estimate, the second gives the precise end-point. In all cases, the insoluble $Hg(MBT)_2$ is obtained. The presence of larger amounts of strong acids is disadvantageous. Large amounts of acetic acid cause disturbances in aqueous solution; dilute alcoholic solution is therefore used. The theoretical end-point is obtained by the intersection of two lines. In acid solution a horizontal maximum density line is obtained at the end of the reaction; in alkaline solution a maximum point is obtained instead. 1-2 mg mercury or mercaptobenzthiazole may be determined in 20-30 ml solution with an error of 0-3%. The titration time is 10-20 minutes.

RÉSUMÉ

Les déterminations hétérométriques du mercure ou du mercaptobenzthiazole sont très sensibles. On emploie une solution aqueuse ou alcoolique diluée. La titration peut être effectuée entre les pH 2 et 10. Lors de la détermination du mercaptobenzothiazole, on obtient deux points finaux, le premier donnant une valeur approximative, le second une valeur précise; dans tous les cas, on obtient le composé $Hg(MBT)_2$, insoluble. La présence de grandes quantités d'acides forts n'est pas favorable. De grandes quantités d'acide acétique gênent en solution aqueuse, c'est pourquoi on utilise une solution alcoolique diluée. Le point final théorique est obtenu par l'intersection de deux lignes. En solution acide on obtient une ligne horizontale à la fin de la réaction, en solution alcaline, par contre, un point maximum. 1-2 mg de mercure ou de mercaptobenzothiazole peuvent être dosés dans 20-30 ml de solution, avec une erreur de 0-3 %. La titration dure 10 à 20 minutes.

ZUSAMMENFASSUNG

Die heterometrische Bestimmung von Quecksilber (II) oder von Mercaptobenzthiazol ist eine sehr empfindliche Reaktion. Es wird in einer wässrigen oder verdünnten alkoholische Lösung bei pH = 2-10 titriert. Bei der Bestimmung von Mercaptobenzthiazol werden zwei analytische Endpunkte erhalten; der erste Punkt dient zur Approximation während der zweite Punkt genau ist. In allen Fällen wird das unlösliche $Hg(MBT)_2$ erhalten. Die Gegenwart von grossen Mengen starker Säuren ist von Nachteil. Grössere Mengen von Essigsäure wirken störend in wässriger Lösung. Man verwendet darum eine verdünnte alkoholische Lösung. Der theore-

References p. 571.

tische Endpunkt ist der Kreuzpunkt von zwei Linien. In saurer Lösung wird eine horizontale Linie der maximalen optischen Dichte erhalten. In alkalischen Lösungen wird dagegen ein Maximum-Punkt erhalten. 1-2 mg Quecksilber oder Mercaptobenzthiazole können in 20-30 ml Lösung mit einem Fehler von 0-3 % bestimmt werden. Die Titrationsdauer ist etwa 10-20 Minuten.

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THE RAPID ESTIMATION OF TITANIUM IN ALLOY STEEL

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The increasing use of titanium in alloy steels makes a rapid method of analysis very desirable for production control. The low concentrations of the element present and the intensity of its coloured complexes strongly favour colorimetric analyses. Many organic compounds have been reported as giving a colour with titanium (salicylic acid, gallic acid, dihydroxymaleic acid[1]; thymol[1,2,3]; disodium 1,2-dihydroxybenzene-3,5-disulphonate[4]; chromotropic acid [5,6]; catechol and ascorbic[7]) but the well established technique is the development of the orange-yellow pertitanyl complex with hydrogen peroxide[1].

Since the major constituents of alloy steels (iron, chromium, nickel and vanadium) are also capable of forming coloured compounds, the final colorimetric evaluation of the titanium must be preceded by some time-consuming operation to remove the interferents or isolate the titanium. Many methods are available but the recommended standard practice is based on a precipitation of the titanium with cupferron[9].

Rapid methods of analysis have been published[10,11] which eliminate preliminary separations by using steels of similar composition as blanks in the colorimetric comparisons but the accuracy of these methods with highly alloyed steels is very doubtful. A modern development is the use of ethylenediaminetetraacetic acid to complex interferants[12,14].

The method described below is an extension of this work and allows titanium to be estimated in stainless steels in approximately half an hour with an accuracy comparable with other techniques.

EXPERIMENTAL

Most of the investigation was concentrated on the analysis of stainless steels containing approximately 18% Cr, 10% Ni and 0.5% Ti but it is felt that the method is applicable to all grades of steel with little modification.

0.25 g of steel were dissolved in 20 ml $5N$ HCl and 5 ml $HClO_4$ and evaporated to strong fumes of perchloric acid (a).

When thoroughly cool, the fumed residue was dissolved in 40 ml of "Vermag" reagent (b) and the solution made ammoniacal with 5*N* NH_4OH (the iron complex going deep red) (c).

After brisk agitation and standing for several minutes, the precipitate present was filtered through a small Buchner funnel and washed thoroughly with water (d).

This precipitate was dissolved in 250 ml of 5% H_2SO_4, the solution being collected in a clean Buchner flask (e).

The titanium colour was developed with hydrogen peroxide and the transmittancy of the solution determined in a Coleman Universal Spectrophotometer using a wavelength of 425 mμ (maximum absorbance of the peroxide colour) and 4 cm cells (f).

Comparison with a calibration graph prepared from a standard titanium solution gave the percentage of titanium in the steel.

Notes on the method

(a) The weight of sample taken will vary with the amount of titanium present in the sample and the intensity of colour required for final evaluation. However, it is advisable to keep the concentration of $HClO_4$ in the fumed residue to a minimum. This may be accomplished by strong fuming or if duplicates are desired, double the weight of steel for the same amount of acid and after dissolving the residue, divide into two equal volumes and continue as above.

(b) The "Vermag" reagent was prepared by dissolving 37.5 g of E.D.T.A. in 5*N* NaOH, the pH of the solution being made just acid to phenolphthalein. 50 g of magnesium sulphate were added and the solution diluted to one litre. The weight of E.D.T.A. added to an estimation must be at least six times the weight of sample taken and hence if larger sample weights are used, the composition of this reagent must be varied accordingly. Cheap, commercial E.D.T.A. was found to be quite satisfactory for this reagent.

(c) Since large excesses of NH_4OH and ammonium salts were found undesirable, the acidity of the solution should be such that little more than 10 ml 5*N* NH_4OH are required for neutralisation. An excess of approximately one quarter the volume of NH_4OH added usually ensures complete titanium recovery.

(d) After agitation and standing, there should be a visible precipitate of titanium magnesium salts. On filtering, this precipitate may be light orange in colour due to adsorption of the chromate ion. Too much free NH_4OH or long periods of standing result in bulky precipitates which are highly contaminated with this ion. The red filtrate should be clear, a Whatman No. 50 filter paper being found sufficiently retentive in most cases.

(e) After solution of the precipitate in sulphuric acid, the filtrate should appear colourless or only very faintly tinged with yellow. A strong yellow colour (in the absence of H_2O_2) indicates excessive chromate contamination and the titanium should be reprecipitated with NaOH and the filtration repeated. Since some

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titanium may adhere to the sides of the original assay flask it is advisable to return the filtrate to this flask to ensure full recovery. The volume of acid used can be varied to give a suitable colour intensity for comparisons.

(f) Transmittancy readings were made using both distilled water and unoxidized filtrate as the comparison blanks. For reasons explained later, chromium contamination gave high results in the former method and low results in the latter but in the presence of moderate contamination both methods were satisfactory.

The analytical results obtained using this method on several standard steels are given in Table I.

TABLE I

% Ti Present	% Ti (a) Found	Mean % Ti Found	% Ti Present	% Ti (b) Found	Mean % Ti Found
0.61	0.615	0.62	0.61	0.580	0.59
	0.615			0.600	
	0.610			0.600	
	0.650			0.580	
	0.620			0.590	
0.36	0.365	0.365	0.36	0.330	0.36
	0.345			0.370	
	0.370			0.370	
	0.380			0.370	
	0.365			0.370	
0.64	0.660	0.65	0.64	0.630	0.61
	0.620			0.630	
	0.625			0.590	
	0.660			0.600	
	0.670			0.610	
0.037	0.040	0.037			
	0.038				
	0.034				

(a) Water used as comparison blank.
(b) Filtrate used in comparison.

DISCUSSION

Although most metals form strong complexes with E.D.T.A., the instability of the titanium in ammoniacal solution is sufficient to allow the titanium to precipitate on standing, which fact has been used in its separation[12]. The precipitation may be speeded up by the addition of ammonium carbonate [13] or magnesium sulphate[14], probably owing to the fact that titanium forms relatively insoluble double sulphates with alkali metals and ammonium ions[15].

In this estimation, it was found most convenient to add the magnesium sulphate with the E.D.T.A. as a combined reagent. The resulting magnesium com-

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plex prevented reduction of the chromate by excess reagent, eliminated possible interaction with excess perchloric acid and reduced the tendency of titanium to form any complex. On making the solution ammoniacal, the magnesium was immediately replaced by the more stable complex ions (iron, nickel *etc.*) and was precipitated (apparently as the hydroxide), this precipitate acting as a carrier for any colloidal, basic titanium salts.

The interference of chromium and manganese which was noted by PŘIBIL[12] can be overcome in the colorimetric method by a preliminary oxidation to the higher valency. This is very conveniently done by using perchloric acid to take the sample into solution.

The effect of the small amount of chromate which becomes adsorbed on the filtered precipitate is further reduced on the addition of the hydrogen peroxide. Chromates react to form an evanescent blue colour which is only slightly absorbed by the wavelength used in the comparison. The small residual absorbance explains the high results obtained using water as the blank and the change in molecular species on the addition of the peroxide is responsible for the low results obtained using the filtrate as the comparison blank.

In both cases however, the accuracy is sufficiently good to warrant industrial application. The variations are of the order of ± 5% and since the method is quick, cheap and simple, the use of duplicates would ensure reliable results. Work now proceeding could provide even greater accuracy.

CONCLUSIONS

The problem of interfering elements in the colorimetric estimation of titanium in alloy steels may be overcome by precipitating this element from an ammoniacal solution containing E.D.T.A. to complex interferants.

The recovery of titanium is virtually complete but the final colorimetric comparison is slightly marred by a small amount of co-precipitated material. Despite this limitation, the method posseses sufficient accuracy, speed and simplicity to suggest its application to routine analysis.

SUMMARY

Titanium in alloy steels has been rapidly estimated with moderate accuracy by taking the steel into solution with perchloric acid and precipitating the element from an ammoniacal solution containing E.D.T.A., magnesium sulphate being used to accelerate precipitation. The Ti was then determined colorimetrically using the yellow colour developed by hydrogen peroxide in acid solutions.

RÉSUMÉ

Le titane dans les aciers peut être dosé rapidement avec une précision suffisante, par attaque de l'échantillon à l'acide perchlorique, et précipitation du titane en solution ammoniacale renfermant E.D.T.A. et du sulfate de magnésium (utilisé pour accélérer la précipitation). Le titane est ensuite dosé colorimétriquement par le peroxyde d'hydrogène.

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ZUSAMMENFASSUNG

Titan kann in Stahllegierungen mit mässiger Genauigkeit schnell bestimmt werden. Nach Auflösen des Stahles in Perchlorsäure wird das Element in einer E.D.T.A. enthaltenden ammonalkalischen Lösung ausgefällt, wobei Magnesiumsulfat verwendet wird, um die ausfällung zu beschleuniger. Titan kann dann in saurer Lösung, mit Hilfe der mit H_2O_2 entstehenden gelben Farbe, kolorimetrisch bestimmt werden.

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A COLORIMETRIC METHOD FOR THE ESTIMATION OF GLUTAMIC ACID IN PROTEIN HYDROLYZATES

by

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It was found by OLCOTT[1] that on autoclaving protein hydrolyzates at pH 3.3 for 4 hours at 125° almost all of the glutamic acid was converted into pyrrolidonecarboxylic acid. The quantity of glutamic acid in the hydrolyzates was estimated by measuring the loss in amino nitrogen caused by this conversion.

We found that pyrrolidonecarboxylic acid could be estimated colorimetrically by heating it with a 50% (w/v) solution of hydroxylamine hydrochloride in $2N$ NaOH and subsequent treatment with ferric chloride as in the procedure used by LIPMANN AND TUTTLE[2] for the estimation of hydroxamic acids. Amounts of pyrrolidonecarboxylic acid ranging from 10 to 50 micromoles could be estimated in this way giving a linear relationship between concentration and optical density. Using this method we estimated the pyrrolidonecarboxylic acid formed from glutamic acid in the autoclaved hydrolyzates of various proteins. The glutamic acid values obtained were in good agreement with those previously obtained by other methods.

EXPERIMENTAL

Hydrolysis and autoclaving

1.5-2 grams of protein were heated under reflux with 20 ml of hydrochloric acid (1 : 1) in a stirred oil bath at a bath temperature of 120-125° for 35 hours. 1 gram of purified bone charcoal was added and heating was continued for 1 hour. After cooling, 10 ml of water were added, the hydrolyzate was filtered and the residue was washed with 25 ml of water. (It was found, in separate experiments, that this treatment with charcoal did not cause a loss of glutamic acid from the hydrolyzates.) The filtrate was adjusted to pH 3-4 with the aid of a glass electrode by addition of $7N$ NaOH and was autoclaved for 4 hours at 125°. Any precipitate was removed by filtration and washed. The total volume was adjusted to 100 ml by addition of water.

Colorimetric procedure

8 ml of the autoclaved hydrolyzate were transferred to a test tube and 4 ml of a 50% (w/v) solution of hydroxylamine hydrochloride in $2N$ NaOH were added.

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The tube was closed with a rubber stopper equipped with a thick-walled capillary tube and was heated for 15 minutes in a boiling water bath. To 1.5 ml of the cooled mixture were then added 1.5 ml of water and 2.5 ml of the ferric chloride reagent consisting of a mixture of equal volumes of 2.5*N* HCl, a 15% solution of trichloroacetic acid, and a 5% solution of ferric chloride in 0.1*N* HCl. The colour produced was immediately measured in a Klett-Summerson photoelectric colorimeter with filter 54. A mixture of 2.5 ml of the ferric chloride reagent and 3 ml of water was used as a blank. No colour was produced when protein hydrolyzates adjusted to pH 3-4 were treated in the same manner without being previously autoclaved.

For comparison, standard solutions of DL-pyrrolidonecarboxylic acid[3] which had been recrystallized from hot water with addition of charcoal were treated in the same manner as the autoclaved hydrolyzates. Typical results are given in Table I. No significant increase in colour was obtained when the solutions of pyrrolidonecarboxylic acid were heated with the hydroxylamine reagent for 20 minutes instead of 15.

TABLE I

COLOUR REACTION BETWEEN FERRIC CHLORIDE AND PYRROLIDONECARBOXYLIC ACID TREATED WITH HYDROXYLAMINE

Pyrrolidonecarboxylic acid, mg	Colorimeter reading
2	95
3	135
4	185
5	224
6	268

Calculation of the results

The results given in Table II were calculated according to the formula

$$\%\ \text{Glutamic acid} = \frac{a \times 1.14 \times 100000}{b \times (100 - m) \times 93.5}$$

a = milligrams of pyrrolidonecarboxylic acid found

b = grams protein in the sample hydrolyzed

m = percentage moisture (estimated by drying the proteins *in vacuo* over phosphorus pentoxide at 100°)

1.14 = the conversion factor from pyrrolidonecarboxylic acid to glutamic acid according to the ratio of their molecular weights

The figure 93.5 was found by us to be the average percentage value for the ring closure of glutamic acid to pyrrolidonecarboxylic acid. This value was the result of 8 separate autoclavings of glutamic acid. OLCOTT[1] used the figure 92.

The figures given in Table II are average values obtained from 3 separate hydrolyses of each protein. The maximum differences between the highest and the lowest values obtained were 10%.

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TABLE II

GLUTAMIC ACID CONTENT OF PROTEINS (PER CENT)

Protein	Found	Previous findings
Casein *	23.1	22.0 (a); 22.4 (b)
Edestin **	20.0	18.3 (a); 19.4 (b)
Zein **	25.3	23.5 (a); 26 (b)
Fibrin **	16.5	16.0 (a); 15.0 (c)
Lactalbumin **	16.6	14.1 (d)

* Fat-free, The British Drug Houses Ltd., London.
** Nutritional Biochemicals Corporation, Cleveland, Ohio.
(a) OLCOTT[1]; (b) Cited from GREENBERG[4]; (c) HIER *et al.*[5]; (d) SAUBERLICH *et al.*[6].

SUMMARY

On heating with hydroxylamine and on subsequent treatment with ferric chloride, pyrrolidonecarboxylic acid gives a colour reaction. This reaction can be used for the quantitative estimation of glutamic acid in protein hydrolyzates since this acid is almost completely converted into pyrrolidonecarboxylic acid at 125° and pH 3-4.

RÉSUMÉ

L'acide pyrrolidonecarboxylique, chauffé en présence d'hydroxylamine et traité ensuite avec le chlorure ferrique, donne une réaction colorée. Cette réaction peut être utilisée pour le dosage de l'acide glutamique dans les protéines hydrolysées, l'acide glutamique étant transformé presque complètement en acide pyrrolidonecarboxylique à la température de 125° et à un pH 3-4.

ZUSAMMENFASSUNG

Pyrrolidoncarbonsäure gibt beim Erhitzen mit Hydroxylamin und nachträglichem Behandeln mit Ferrichlorid eine Farbreaktion. Da Glutaminsäure beim Erhitzen auf 125° bei pH 3-4 fast vollständig in Pyrrolidoncarbonsäure verwandelt wird, kann diese Farbreaktion zur quantitativen Bestimmung von Glutaminsäure in Proteinhydrolysaten verwendet werden.

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QUANTITATIVE BESTIMMUNG VON KOBALT AN DER ROTIERENDEN QUECKSILBERELEKTRODE *

von

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Die rotierende Quecksilberelektrode[13,14,10,15], mit der sehr gute Resultate bei der quantitativen Bestimmung von Zink, Chrom, Quecksilber und Kupfer erzielt wurden und die dabei ihre Vorzüge vor den unbeweglichen Quecksilberelektroden bewiesen hatte, wurde in modifizierter Ausführung auch für die elektroanalytische quantitative Kobaltbestimmung angewandt.

Nach SCHLEICHER[12] kann Kobalt galvanoelektrisch bestimmt werden und nach FISCHER UND BRUYLANTS[2], JILEK UND VRESDAL[5] und anderen wird Kobalt an einer Platinelektrode aus ammoniakalischer Lösung unter beschränkter Stromspannung oder mit konstantem Potential unter Zugabe von Reduktionsmitteln, am häufigsten unter Verwendung von Hydrazinsulfat, bestimmt. Der erschwerende Umstand dabei ist das nötige elektrolytische Überziehen der Platinkathode mit Kupfer. Bei der Ausführung schneller analytischer Bestimmungen, bei etwa 1400 Umdrehungen des Rührers in einer Minute, können etwa 100 mg Kobalt mit einer Stromstärke von 0.5 bis 1.5 A in etwa 90 Minuten quantitativ abgeschieden werden. Bei mässigerem Rühren, mit etwa 800 Umdrehungen in der Minute, dauern diese Bestimmungen ungefähr 180 Minuten, auch bei Anwendung grösserer Stromstärken.

An einer ruhenden Quecksilberkathode kann nach PAWECK UND WALTHER[11], sowie nach BÖTTGER[1] Kobalt auch in schwefelsauren, salpetersauren und chlorwasserstoffsauren Lösungen unter anodischem Rühren bestimmt werden. Nach BÖTTGER[1] hat die systematische Nachprüfung dieser Methode gezeigt, dass die Resultate die mit der Quecksilberkathode erreicht werden, in der Regel um etwa 1% niedriger sind als diejenigen die an der Platinkathode unter Zugabe von Hydrazinsulfat erzielt werden, während LUKENS[9] an der Quecksilberkathode immer zu etwas höheren Resultaten kommt.

Wir haben Kobalt an der rotierenden Quecksilberkathode, bestehend aus einem Glasschälchen, angeschmolzen an ein Glasrohr das als Achse dient, durch die von dem Aufsatz aus Leichtmetall die elektrische Leitung zum Quecksilber bewirkt wird, quantitativ bestimmt[13,14,10,15]. Durch den erwähnten Aufsatz aus Leichtmetall kann die rotierende Elektrode an die Achse des Rührmotors befestigt und rotiert werden, wobei durch die Zentrifugalkraft der Drehung die Quecksilberoberfläche bedeutend vergrössert wird. Als Anode dient eine horizontale Platindrahtspirale oder Platinnetzelektrode. Die beiden Elektroden werden nach der Vorbereitung in die zu untersuchende Lösung eingeführt, die sich in einem geeigneten Glasbecher befindet, in dem auch die Bestimmung ausgeführt wird. Auf diese Weise können schwer mit der ursprünglichen rotierenden Quecksilberelektrode befriedigende Stromstärke und günstige Dauer der Kobaltbestimmung erzielt werden, aber die erhaltenen Resultate bewegen sich, bei genügender Verlängerung der Bestimmung, in erlaubten analytischen Fehlergrenzen, oder stimmen mit den Resultaten die an der Platinkathode oder gravimetrisch paralell erzielt werden, überein.

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Um die gewünschte Stromstärke und eine wesentliche Verkürzung der Bestimmungsdauer zu erreichen, wurde die ursprüngliche rotierende Quecksilberelektrode derart modifiziert, dass durch Vergrösserung des Quecksilberschälchens die Elektrolyse der zu untersuchenden Lösung in ihr selbst ermöglicht wurde, wodurch die Metallionenbestimmung in der rotierenden Elektrode, die auch die Anode in sich aufnimmt, mit weit grösserer Stromstärke und mit bedeutend kürzerer Zeitdauer ausgeführt werden konnte (Fig. 1).

Durch diese Vergrösserung des Glasschälchens konnte die rotierende Quecksilberelektrode nicht nur als rotierendes Quecksilbergefäss, sondern auch als Katholytbehälter, in dem die Elektrolyse ausgeführt wird, gebraucht werden, so dass dadurch der Becher als ursprüngliches Elektrolysengefäss vollständig weggelassen werden konnte. Die Ausmasse und das Volumen des ursprünglichen Glasschälchens sind so bemessen, dass kein Verspritzen des Elektrolyten beim Rotieren der Elektrode zu befürchten ist.

Als Anode wurde eine Platindrahtspirale benutzt, die in den Elektrolyten im Quecksilberschälchen über dem Kathodenquecksilber eingeführt werden konnte. Durch Änderung des Abstandes zwischen der Platinanode und der Quecksilberoberfläche

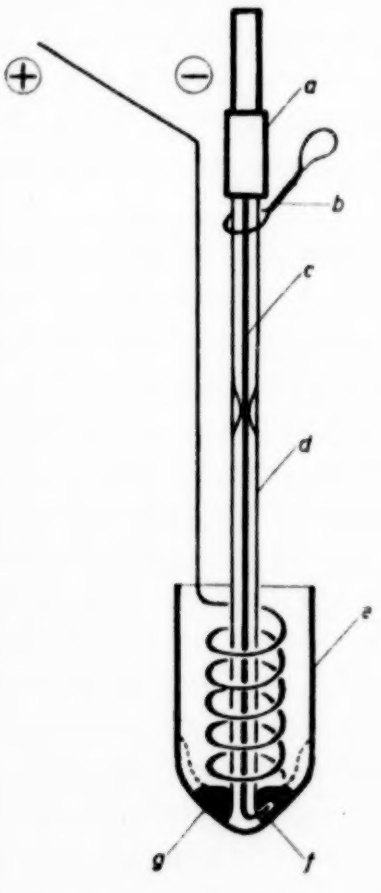

Fig. 1. Modifizierte rotierende Quecksilberelektrode *a* Aufsatz aus Leichtmetall, *b* Platindraht *c* Kupferdraht, *d* Glasrohr, *e* Glasschale *f*, Platindrahtspitze, *g* Quecksilber

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konnten der günstige Elektrolytwiderstand eingestellt und die gewünsch e Stromstärke erreicht werden.

Im Vergleich mit der ursprünglichen rotierenden Quecksilberelektrode[13,14,10,15] hat diese modifizierte Elektrode noch den Vorteil, dass aus ihr nach Beendigung der Elektrolyse, ohne die Anode herauszunehmen und den Strom zu unterbrechen, der Elektrolyt durch eine krumme, mit einer Verbreitung versehene Pipette bis zum letzten Tropfen ohne Mühe herausgesaugt werden kann. Als weiterer Vorzug dieser modifizierten rotierenden Quecksilberelektrode kann auch das Arbeiten mit kleinen Volumina des Elektrolyten angesehen werden, so dass für eine Bestimmung meistens nur etwa 10-15 ml, höchstens 20 ml, von der zu untersuchenden Lösung benötigt werden.

Durch erreichbare grössere Stromstärken, durch inniges Mischen und stark gesteigertes Eindringen des gebildeten Amalgams in das Innere der Quecksilbermasse wurde ermöglicht, die Zeit für eine quantitative Abscheidung der an der Quecksilberkathode zu bestimmenden Metallionen bedeutend zu verkürzen. Intensives Durchmischen des Quecksilbers durch das Rotieren der Elektrode hat auch einen günstigen Einfluss auf die Erhaltung hoher Überspannung des Wasserstoffs am Kathodenquecksilber, die bedeutend verkleinert wird im Falle, dass das abgeschiedene Metall nicht von der Quecksilberoberfläche genügend schnell in das Innere befördert wird.

Bei der Kobaltbestimmung betrug die benötigte Quecksilbermenge in dieser modifizierten Quecksilberelektrode 16 bis 25 g, während KOLLOCK UND SMITH[6] etwa 40 bis 50 g Quecksilber gebrauchten. Die Bestimmungen wurden in etwa 10 bis 15 ml Kobaltsulfatlösungen ausgeführt, unter Zugabe von etwa 0.1 ml konzentrierter Schwefelsäure. Für quantitative Abscheidung von 27.4 mg bis 216.3 mg Kobalt benötigt man, unter den angegebenen Bedingungen, 40-70 Minuten. Zugabe grösserer Mengen Schwefelsäure übt einen ungünstigen Einfluss aus und erleichtert stärkere Wasserstoffabscheidung, was zu unnötiger Verlänggerung der Kobaltbestimmung führt. Das Rotieren der Quecksilberkathode darf während der Bestimmung nicht unterbrochen werden, da es sonst zur Abscheidung von schwammigem Kobalt und Amalgam kommt, die in dieser Form auch weiter bis zum Ende der Bestimmung bestehen bleiben und sich sehr schwer auswaschen lassen, was unrichtige Resultate ergibt. Trotz sehr kleiner Löslichkeit des Kobalts in Quecksilber, die nach IRVIN UND RUSSELL[4] etwa $8 \cdot 10^{-5}$ % beträgt, ist das erhaltene Amalgam glänzend und homogen und kann ohne Schwierigkeiten gewaschen und mittels Aceton getrocknet werden. Durch Luftsauerstoff wird das erhaltene Amalgam allmählich oxydiert und nach einigen Stunden scheidet sich auf der Oberfläche ein feinpulveriges, schwarzes Kobaltoxyd ab. Die Elektrolysen wurden mit Stromstärken von etwa 2 A ausgeführt, wobei es auch zu intensiver Wasserstoffabscheidung und Erwärmung des Elektrolyten kommt. Obwohl die erhöhte Temperatur einen günstigen Einfluss auf die Kobaltabscheidung ausübt, kann nötigenfalls während des Arbeitens auch eine Kühlung der

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rotierenden Elektrode durch Unterstellen eines Wasserbehälters, bequem bewirkt werden.

Bei der elektrolytischen Abscheidung von Kobalt aus schwefelsauren Lösungen geht die rötliche Färbung der Lösung in dunkelrot und violett über, die unter unseren Arbeitsbedingungen nach etwa 10-15 Minuten verschwindet und die Lösung farblos wird, was zu falschen Schlüssen in Bezug auf das Ende der quantitativen Bestimmung führen kann. Die erwähnte Farbänderung des Elektrolyten während der Elektrolyse noch vor Erreichung auch nur annähernd vollständiger Abscheidung des Kobalts hat schon BÖTTGER[1] beobachtet. KOLLOCK UND SMITH[6], die eingehend den zeitlichen Verlauf der elektrolytischen Kobaltabscheidung, bei verschiedenen Stromstärken und bei verschiedenen Konzentrationen studierten, bewiesen einwandfrei die sehr träge Abscheidung der letzten Spuren von Metallionen, was auch wir durch unsere Untersuchungen bestättigen konnten. Für die Kontrolle der quantitativen Abscheidung von Kobalt an der Quecksilberkathode bedienten wir uns nach KORENMAN[8,16] mit Erfolg des Ammoniummercurirhodanids unter Zugabe von Zinksulfat, mit dem Kobalt einen blauen kristallinischen Niederschlag der Mischverbindung $Co[Hg(CNS)_4]\cdot Zn[Hg(CNS)_4]$ bildet, wobei die Anwesenheit von Zink die Empfindlichkeit der Reaktion bis auf $D = 10^{-5.7}$ erhöht.

Quantitative Kobaltbestimmungen an der modifizierten rotierenden Quecksilberelektrode wurden unter verschiedenen Bedingungen der Stromstärke und der Mengen von Schwefelsäure ausgeführt. Die besten Resultate erzielt man bei Zugabe von 0.1 ml konzentrierter Schwefelsäure zu 10-15 ml des zu untersuchenden Elektrolyten und bei Anwendung von Stromstärken um 2 A. Wie aus der Tabelle I zu ersehen ist, bewegte sich der Fehler der quantitativen Bestimmungen von Kobalt zwischen 0.12 und 0.29 %. Die in der Tabelle angeführten Resultate sind Mittelwerte von mindestens 6 Einzelbestimmungen.

Die Eichung der untersuchten Kobaltsulfatlösungen erfolgte durch elektroanalytische Bestimmung nach KOLLOCK UND SMITH[7] aus ammoniakalischen

TABELLE I

Genommen Kobalt	Gefunden Kobalt	Fehler		Volumen	Schwefels. konz.	Stromstärke	Dauer der Bestimmung
mg	mg	mg	%	ml	ml	A	Min
216.5	216.3	0.6	0.29	20	0.2	2.5	75
216.9	216.4	0.5	0.24	20	0.2	2.5	70
162.4	162.2	0.2	0.12	15	0.1	2.0	50
162.4	162.0	0.4	0.24	15	0.1	2.0	55
162.4	162.1	0.3	0.18	15	0.1	2.0	50
162.4	162.0	0.4	0.24	15	0.1	2.0	50
162.4	162.1	0.3	0.18	15	0.1	2.0	50
27.4	27.4	—	—	10	0.05	1-1.5	40

Lösungen unter Zugabe bestimmter Menge Ameisensäure, mit dem Unterschied, dass anstelle einer rotierenden Platinspiralanode und einer Platinschale als Kathode, eine Winkler'sche mit Kupfer überzogene Elektrode als Kathode gebraucht wurde. Die Bestimmungen wurden mit Stromstärken von 2 A, anstelle mit 6.5 A ausgeführt. Die erhaltenen Resultate wurden ausserdem durch gravimetrische Bestimmungen von Kobalt als Pyrophosphat kontrolliert.

ZUSAMMENFASSUNG

Es wurde eine modifizierte rotierende Quecksilberelektrode, die zu gleicher Zeit als Kathode und als Behälter für den Elektrolyten dient, konstruiert, und ihre Wirkungsweise sowie die Vorteile anderen Quecksilberelektroden gegenüber an der quantitativen Kobaltbestimmung studiert.

An dieser modifizierten Quecksilberelektrode konnten mit Verkürzung der Elektrolysendauer quantitative Kobaltbestimmungen ausgeführt werden, wobei unter Einhalten bestimmter Bedingungen, trotz leichter nachträglicher Oxydierbarkeit des Kobalts aus dem Amalgam, befriedigende Resultate erreicht werden können, was zur Empfehlung der rotierenden Quecksilberelektrode und der beschriebenen Methode für die quantitative Kobaltbestimmung berechtigt.

SUMMARY

A modified mercury electrode was constructed and used as a cathode and, at the same time, as a container for the electrolyte. Its applicability as well as its advantages in comparison with other mercury electrodes have been studied on the determination of cobalt.

On this rotating electrode cobalt could be quantitatively determined with a shorter duration of electrolysis. If determined conditions were fulfilled, satisfactory results could be obtained in spite of a slight tendency for a subsequent oxidation of the cobalt from the amalgam. This justifies the recommendation of the rotating mercury electrode and of the method described for the quantitative determination of cobalt.

RÉSUMÉ

Une électrode rotative à mercure modifiée a été construite, servant simultanément de cathode et de récipient pour l'électrolyte. Son fonctionnement et ses avantages sur les autres électrodes à mercure ont été étudiés lors du dosage du cobalt. Grâce à cette électrode rotative, il a été possible de diminuer la durée d'électrolyse. Dans des conditions déterminées, des résultats satisfaisants ont pu être obtenus, malgré la facilité avec laquelle le cobalt amalgamé, peut s'oxyder ultérieurement. L'emploi d'une telle électrode, de même que la méthode décrite, peuvent donc être recommandés pour le dosage du cobalt.

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THE OXIDATION OF THALLIUM(I) BY ALKALINE FERRICYANIDE

by

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Powerful oxidising agents, under certain experimental conditions, oxidise thallous salts to the thallic state and these redox reactions have been adopted successfully for the quantitative determination of thallium[1,2]. With the exception of KIO_3, other oxidants were, however, found to be unsatisfactory for an accurate titrimetric analysis. Electrometric methods have therefore received more attention recently and have yielded better results than those obtained by direct titrations[3-7]. MIURA determined thallium by titrating Tl(I) potentiometrically in a strong alkaline medium against potassium ferricyanide at elevated temperatures[8]. Attempts made to employ this technique, however, showed variable results presumably due to the partial oxidation of the ferrocyanide formed during the reaction especially when the temperature was maintained at or above 60° C. A modified procedure was therefore worked out by using sodium arsenite as a primary standard for the potentiometric estimation of the excess ferricyanide. The present communication describes the applicability of this simple method for the quantitative determination of thallium.

EXPERIMENTAL

Merck's reagent grade sample of thallous acetate was used to prepare solutions of various concentrations. The thallium content of an aliquot portion of the solution was determined by the classical iodate method[2]. To 10 ml of the thallous solution an excess of $K_3[Fe(CN)_6]$ was added, followed by a concentrated (30%) solution of NaOH. The overall concentration of the alkali was maintained at or above 8*N*. A deep brown precipitate of thallic hydroxide was obtained immediately on the addition of alkali. This was stirred thoroughly and, without filtering the precipitate, the excess ferricyanide was titrated potentiometrically at room temperature against standard sodium arsenite. A sharp break in the potential was observed when the ferricyanide was reduced quantitatively to $K_4[Fe(CN)_6]$ according to the reaction:

$$4K_3[Fe(CN)_6] + As_2O_3 + 4KOH \rightarrow 4K_4[Fe(CN)_6] + As_2O_5 + 2H_2O \qquad (1)$$

The end-point was also characterized by the complete fading of the yellow colour of ferricyanide to a clear solution in which the brown $Tl(OH)_3$ remained dispersed. A parallel blank titration was carried out to determine the concentration of ferricyanide in terms of the same standard arsenite solution.

The oxidation of Tl(I) to Tl(III) by alkaline ferricyanide is represented by the reaction:

$$Tl_2O + 4K_3[Fe(CN)_6] + 4KOH \rightarrow 4K_4[Fe(CN)_6] + Tl_2O_3 + 2H_2O \qquad (2)$$

The difference in the initial As_2O_3 titre value for ferricyanide and that obtained for its excess after the complete precipitation of $Tl(OH)_3$ gives the quantity of As_2O_3 equivalent to the $K_3[Fe(CN)_6]$ consumed during the oxidation reaction (II). From this the amount of thallium is calculated on the basis: 1 ml of 0.1 *N* As_2O_3 = 0.01022 g Tl.

A typical set of observations is returned in Table I.

TABLE I

Expt. No.	Vol. of $K_3[Fe(CN)_6]$ ml	Vol. of Tl(I) ml	0.1 *N* As_2O_3 equivalent to $K_3[Fe(CN)_6]$ consumed ml	Wt of Tl g		Diff.
				by KIO_3	by As_2O_3	
1	10.0	5.0	2.6	0.02678	0.02658	−0.0002
2	20.0	10.0	3.2	0.03270	0.03277	+0.00007
3	30.0	10.0	7.4	0.07590	0.07561	−0.00021
4	25.0	20.0	14.9	0.1518	0.1523	+0.0005
5	30.0	25.0	18.5	0.1898	0.1891	−0.0007
6	40.0	30.0	22.3	0.2276	0.2279	+0.0003
7	40.0	30.0	27.9	0.2856	0.2851	−0.0005
8	50.0	40.0	31.45	0.3218	0.3214	−0.0004

It may be mentioned that the above experimental technique is essentially a useful application of KOLTHOFF's observation on the potentiometric determination of trivalent arsenic by alkaline ferricyanide[9]. BERRY[10] investigated the reduction of trivalent thallium by arsenious oxide. His results show that freshly precipitated thallium hydroxide oxidises As(III) to As(V) in alkaline medium and the reaction

$$Tl_2O_3 + As_2O_3 \rightarrow Tl_2O + As_2O_5$$

forms the basis of the determination of thallium. Since in the present series of experiments, sodium arsenite is run into a strongly alkaline medium containing excess ferricyanide and thallic hydroxide, a simultaneous reduction of both by the arsenite may be anticipated. This should also lead to the gradual dissolution of thallic hydroxide along with the fading of the colour of ferricyanide. Alternatively, if the two reduction processes $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ and Tl^{+3}/Tl^{+} proceed in successive stages, two breaks in potential should result on addition of appropriate quantities of As_2O_3. In actual experiments, however, only one sharp break was observed at a point when the ferricyanide was reduced completely

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to $K_4[Fe(CN)_6]$. The thallic hydroxide was unaffected even on addition of further quantities of arsenite solution and the change in potential was negligible and obscure. This may be attributed to the fact that the reduction of Tl(III) by trivalent arsenic occurs only at elevated temperatures[10], a condition not essential for the conversion of ferri to ferrocyanide. As a further proof of the validity of the above assumption, the thallic hydroxide was filtered after reduction of $K_3[Fe(CN)_6]$ by an appropriate quantity of As_2O_3. The precipitate was washed thoroughly, dissolved in a minimum quantity of HCl and the thallium content was determined iodometrically[6]. This corresponded to the amount taken initially for precipitation with alkaline ferricyanide. It is therefore evident (Table I) that under the given operative conditions sodium arsenite may be used as a direct primary standard for the quantitative determination of thallium.

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SUMMARY

A simple method for the potentiometric determination of thallium is described. This is based essentially on the precipitation of thallic hydroxide by alkaline ferricyanide and the back titration of excess $K_3[Fe(CN)_6]$ by standard sodium arsenite according to KOLTHOFF's method. Under the specified experimental conditions the reduction of trivalent thallium is not effected by As_2O_3 and the procedure offers therefore a unique advantage of simplicity and accuracy.

RÉSUMÉ

Une méthode simple est décrite pour doser potentiométriquement le thallium(I). On précipite l'hydroxyde de thallium(III) par un ferricyanure en solution alcaline et on titre l'excès de $K_3[Fe(CN)_6]$ par une solution étalon d'arsénite de sodium, d'après la méthode de KOLTHOFF. Dans les conditions de l'analyse, le thallium(III) n'est pas réduit par As_2O_3. Ce procédé présente l'avantage d'être simple et précis.

ZUSAMMENFASSUNG

Es wird eine einfache Methode beschrieben, um das Thallium(I) potentiometrisch zu bestimmen. Man fällt das Thallium(III)-hydroxyd mit einem Ferricyanid in einer alkalischen Lösung und man titriert den Überschuss von $K_3[Fe(CN)_6]$ mit einer Vergleichslösung von Natriumarsenit, nach der Methode von KOLTHOFF. In der Analysenbedingung, wird das Thallium(III) durch As_2O_3 nicht reduziert. Dieser Vorgang bietet den Vorteil einfach und genau zu sein.

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THE RARE EARTHS
A POLAROGRAPHIC STUDY

by

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The rare-earth atoms exhibit slight differences in their electronic structures; thus the 5 d electron is present only in lanthanum, gadolinium and lutecium[1]. One expects these differences to be reflected in the properties of the ions, particularly the deposition potentials of the elements. While the actual deposition potentials are difficult to observe, the dropping mercury electrode records potentials of the same order and may be expected to give an insight into the mechanism of the discharge $M^{+3} \rightarrow M^{\circ}$.

NODDACK AND BRUKL[2] concluded from their studies on the sulphates of Sc, Y and most rare-earth elements, that there is a two-step reduction from $^{+}3$ to $^{+}2$ state and finally to the metal. These findings could not be confirmed by later workers[3], except in the case of the elements europium, samarium and ytterbium — whose divalent salts are definitely known[4]. In the following pages the results of studies on the chlorides of elements, Sc, Y, La, Pr, Nd, Sm, Gd and Dy in lithium chloride, under carefully controlled conditions of pH and concentration of the reducible ion, are presented. It will be noticed that while scandium, in agreement with the observations of LEACH AND TERREY[3], shows only a single reduction wave all other elements present double waves. The position and characteristics of these waves are also discussed.

EXPERIMENTAL

A Cambridge recording polarograph (photographic model) was used. The cathode potential was obtained both by direct measurement with a modified Leeds and Northrup K type potentiometer in conjunction with a reflecting galvanometer of sensitivity $0.30 \cdot 10^{-8}$ amp per mm at 1 metre distance, and also from the applied potential, anode potential and $i \times R$. The two methods gave the same significant values. The resistance of the cell was small and varied in the extremes between 500-600 ohms as measured with a Philips a/c bridge.

pH measurements were made with a Cambridge bench type meter.

The rare-earth chlorides were prepared from spec-pure samples of oxides supplied by Johnson Mathey Co., Ltd., London, and highly purified hydrochloric acid. Double-distilled conductivity water was employed for solution and dilution. pH adjustment was made with addition of lithium hydroxide or hydrochloric acid as required.

The indifferent electrolyte was always 0.1*N* lithium chloride prepared from the purest carbonate and hydrochloric acid.

0.01 per cent gelatin prepared according to KOLTHOFF AND LINGANE[9] was used wherever indicated. The drop time varied from 2.5 to 6 seconds at applied potentials of —2.1 and —0.9 v *vs.* S.C.E. respectively and the factor $m^{2/3}\,t^{1/6}$ from 1.244 and 1.483 $\mathrm{mg}^{2/3}$ Sec $-\frac{1}{2}$ in the same potential range.

The recording galvanometer shows a deflection of one division on the record for $0.521 \cdot 10^{-8}$ amp. Nitrogen for removing oxygen was prepared by the method of TRAVERS[5] and stored in a glass gas-holder. Before entering the electrolytic cell, it was bubbled through wash bottles containing dilute KOH and double-distilled water. The gas was led through the solution for 15-20 minutes at 100-120 bubbles a minute. After turning off the gas, the solution was left for 15 minutes before a potential was applied.

The polarograph has two speeds — both were used as occasion required. It has also a reverse drive which permitted retracing the waves to show absence of lag. An important feature noted in this work with the rare-earths was that the reverse wave, particularly in the second stage of reduction, made a loop with the forward wave thus indicating the irreversibility of the process.

Typical polarograms are presented in Figs. 1-9.

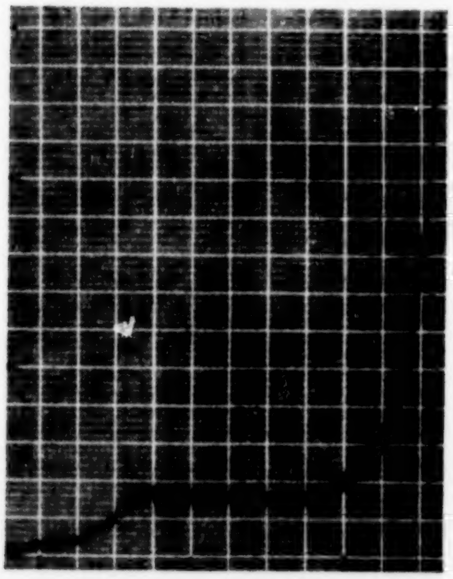

Fig. 1. Supporting electrolyte + suppressor pH 3.12.

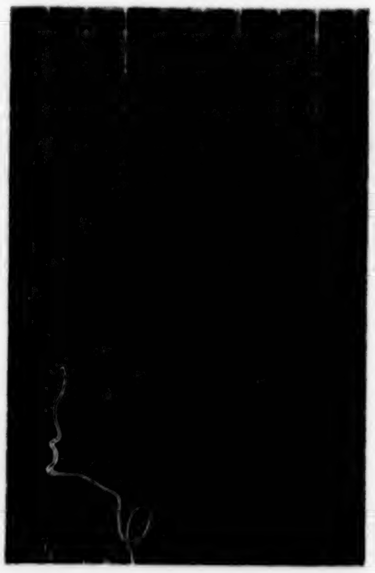

Fig. 2. 1.8 $LaCl_3$ pH 2.84 Ea$\frac{1}{2}$ —1.93V; Eb$\frac{1}{2}$ —2.05 V; *vs.* S.C.E.

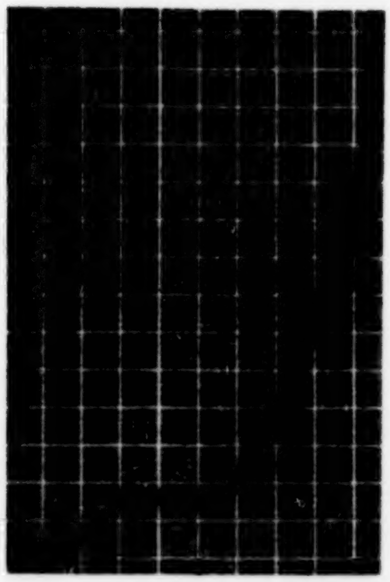

Fig. 3. 1.8 $PrCl_3$ pH 3.10 Ea$\frac{1}{2}$ — 1.85 V; Eb$\frac{1}{2}$ — 2.00 V; *vs.* S.C.E.

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Description of Figures 1-9. Concentration of metal ion in millimoles litre^{-1}. Supporting electrolyte 0.1 *M* lithium/chloride.
Maximum suppressor 0.01 % gelatin.
Temp. 30° ± 0.5 C.
Galvanometer sensitivity 1/200.

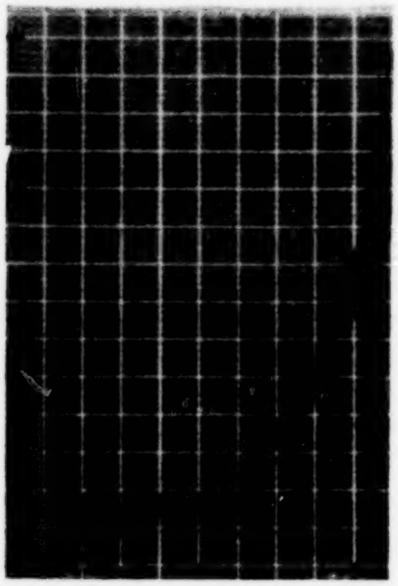

Fig. 4. 1.8 $NdCl_3$ pH 3.07. $Ea_{\frac{1}{2}}$ — 1.85 V; $Eb_{\frac{1}{2}}$ — 2.01 V; *vs.* S.C.E.

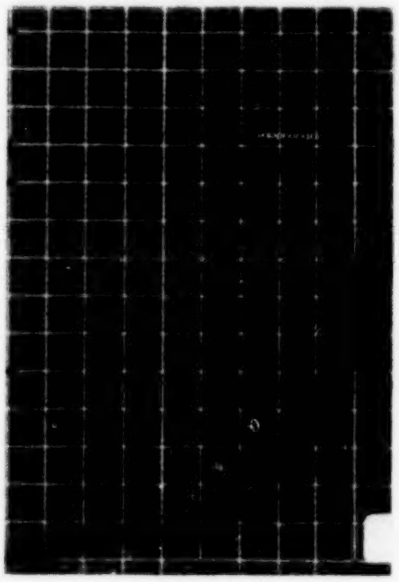

Fig. 5. 1.8 $SmCl_3$ pH 3.41 $Ea_{\frac{1}{2}}$ — 1.80 V; $Eb_{\frac{1}{2}}$ — 1.96 V; *vs.* S.C.E.

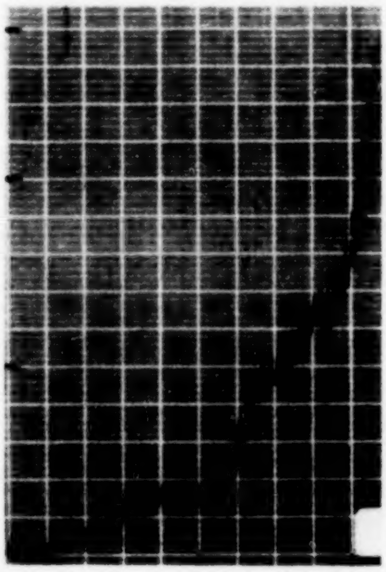

Fig. 6. 1.986 $GdCl_3$ pH 3.10 $Ea_{\frac{1}{2}}$ — 1.85 V; $Eb_{\frac{1}{2}}$ — 1.99 V; *vs.* S.C.E.

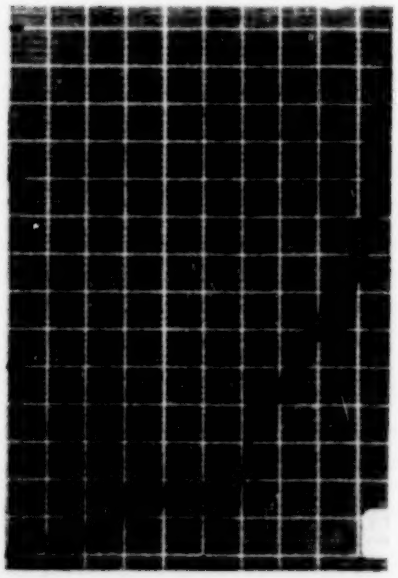

Fig. 7. 3.218 $DyCl_3$ pH 3.09 $Ea_{\frac{1}{2}}$ — 1.79 V; $Eb_{\frac{1}{2}}$ — 1.95 V; *vs.* S.C.E.

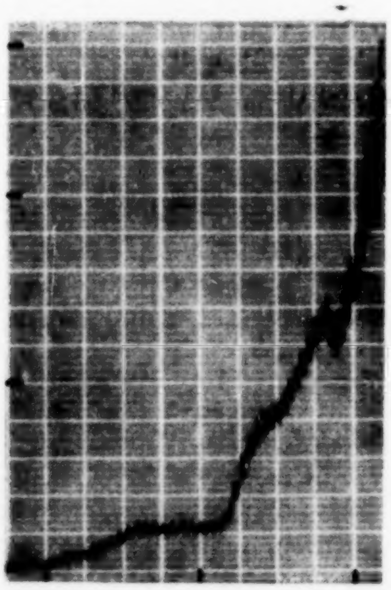

Fig. 8. 2.678 YCl_3 pH 3.27 $Ea_{\frac{1}{2}}$ — 1.83 V; $Eb_{\frac{1}{2}}$ — 1.980 V; *vs.* S.C.E.

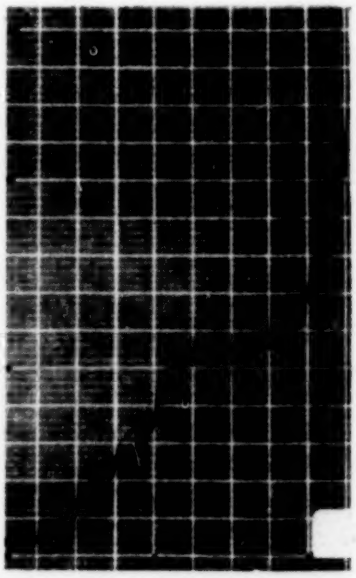

Fig. 9. Very dilute solution of $ScCl_3$ pH 3.12 $E_{\frac{1}{2}}$ — 1.69 V; *vs.* S.C.E.

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Results of study of variation in concentration and pH are shown in the following tables.

TABLE I

VARIATION OF i_d AND $E\frac{1}{2}$ WITH pH

pH	i_{d_1}	i_{d_2}	$E\frac{1}{2}$ *vs.* S.C.E. Ea½	Eb½
	µA	µA	Volts	Volts
(a) Lanthanum. Concn. $1.8 \cdot 10^{-3} M$				
4.94	steps not properly resolved		—1.96	
3.75	8.84	17.16	—1.865	—2.00
3.16	8.84	17.68	—1.895	—2.03
2.74	8.84	17.68	—1.938	—2.07
(b) Praseodymium $1.8 \cdot 10^{-3} M$				
5.60	8.32	15.6	—1.78	—1.96
3.84	8.32	15.6	—1.80	—1.96
3.10	9.36	18.2	—1.846	—1.995
2.76	9.36	17.16	—1.88	—2.035
(c) Neodymium $1.8 \cdot 10^{-3} M$				
5.70	8.32	16.12	—1.81	—1.935
3.78	8.84	18.72	—1.82	—1.995
3.07	9.36	19.24	—1.85	—2.014
2.38	9.36	18.72	—1.86	—2.024
(d) Samarium $1.8 \cdot 10^{-3} M$				
3.72	8.32	13.52	—1.768	—1.947
3.25	8.84	13.00	—1.808	—1.960
3.10	9.36	13.52	—1.818	—1.985
2.76	9.36	11.44	—1.845	—2.005
(e) Gadolinium $1.986 \cdot 10^{-3} M$				
4.94	9.36	11.96	—1.81	—1.97
3.10	10.40	12.48	—1.852	—1.99
2.71	9.88	14.04	—1.882	—2.027
(f) Dysprosium $1.931 \cdot 10^{-3} M$				
5.55	8.84	8.32	—1.743	—1.922
3.09	9.88	9.88	—1.793	—1.941
2.81	9.88	8.32	—1.823	—1.970
(g) Yttrium $1.34 \cdot 10^{-3} M$				
4.91	5.72	10.4	—1.775	—1.956
3.55	5.72	10.92	—1.785	—1.956
3.08	6.76	11.44	—1.846	—1.983
2.72	7.28	11.44	—1.875	—2.019

TABLE II

VARIATION OF i_d AND $E_{\frac{1}{2}}$ WITH CONCENTRATION OF THE REDUCIBLE ION

(a) Lanthanum pH = 2.97

Concn. of R^{+3}	i_{d_1}	i_{d_2}	$\frac{i_{d_1}}{C}$	$E_{\frac{1}{2}}$ *vs.* S.C.E. $Ea_{\frac{1}{2}}$	$Eb_{\frac{1}{2}}$
millimoles/litre	μA	μA	μA millimoles/litre	volts	volts
1.2	5.72	14.04 Maximum	4.77	—1.915	—2.039
1.8	8.84	17.16	4.91	—1.906	—2.030
2.4	11.44	21.84	4.77	—1.906	—2.039
3.0	14.04	28.08	4.68	—1.910	—2.046
(b) Praseodymium pH = 3.10					
1.2	5.72	11.96	4.77	—1.846	—1.995
1.8	9.36	18.20	5.20	—1.846	—1.995
2.4	11.96	23.40	4.98	—1.846	—1.995
3.0	15.08	28.08	5.03	—1.850	—2.020
(c) Neodymium pH = 3.29					
1.2	5.72	11.96	4.77	—1.834	—1.987
1.8	8.84	18.20	4.91	—1.830	—1.995
2.4	11.96	22.36	4.98	—1.834	—1.995
3.0	15.08	25.48	5.03	—1.830	—2.004
(d) Samarium pH = 3.41					
0.8	3.90	7.80	4.875	—1.788	—1.947
1.2	5.72	11.96	4.77	—1.798	—1.956
1.8	8.84	11.96	4.91	—1.798	—1.956
2.4	11.96	14.56	4.98	—1.798	—1.956
3.0	15.08	17.68	5.03	—1.808	—1.976
(e) Gadolinium pH = 3.10					
0.883	4.68	9.36	5.30	—1.852	—1.989
1.324	6.76	10.10	5.11	—1.852	—1.989
1.986	10.40	12.48	5.24	—1.852	—1.989
2.648	14.04	13.52	5.30	—1.852	—1.989
3.310	17.68	16.12	5.34	—1.852	—1.998
(f) Dysprosium pH = 3.09					
0.858	4.16	8.32	4.85	—1.793	—1.941
1.287	6.24	8.32	4.85	—1.793	—1.941
1.931	9.88	9.36	5.12	—1.793	—1.941
2.574	13.00	10.92	5.05	—1.793	—1.941
3.218	16.64	10.92	5.17	—1.793	—1.950

(g) Yttrium pH = 3.27

Concn. of R^{+3}	i_{d_1}	i_{d_2}	$\frac{i_{d_1}}{C}$	$E_{\frac{1}{2}}$ *vs.* S.C.E. $Ea_{\frac{1}{2}}$	$Eb_{\frac{1}{2}}$
millimoles/ litre	μA	μA	μA millimoles/litre	volts	volts
0.670	3.64	7.28	5.43	—1.826	—1.964
1.005	5.20	9.88	5.18	—1.826	—1.964
1.340	6.76	9.88	5.04	—1.826	—1.964
2.010	10.92	11.96	5.43	—1.826	—1.960
2.680	14.56	15.08	5.43	—1.826	—1.980

During these studies it was noticed that the pH of the solution increased after a run due to unmistakable occurrence of an irreversible reduction reaction in which OH^- ions are liberated. The change in pH is sometimes large as may be seen from Table III.

TABLE III

CHANGE IN pH DURING REDUCTION AT THE DROPPING MERCURY ELECTRODE

Electrolyte: Praseodymium chloride in 0.1 *M* LiCl.

Concn. Pr^{+3}	pH Initial	After a run	Remarks
millimoles/litre			
1.2	5.83	6.54	Contains agar
1.2	5.84	6.54	Contains gelatin
1.2	3.24	3.34	No suppressor
1.2	2.96	3.12	Contains gelatin
1.2	2.71	2.88	No suppressor
1.8	3.05	3.23	,, ,,

On a consideration of results in Tables I and II it is evident that
(a) the half-wave potentials shift to more negative values with fall in pH but are independent of concentration in the range 1 to 3 millimoles.
(b) the diffusion current is practically independent of pH.
(c) i_{d_1} (the diffusion current in the first stage of reduction) is proportional to concentration while i_{d_2} (the same in the second or final reduction) shows anomalies with Sm, Gd, Dy and Y-elements of lower basicity.
(d) proportionality between i_{d_1} and i_{d_2} considered as processes of reduction from $^{+}3$ to $^{+}2$ and finally to metal (*i.e.* the ratio $i_{d_1}/i_{d_2} = 2$) may be observed with La, Nd and Pr at all concentrations studied and with Sm, Gd, Dy and Y at

1.2, 0.883, 0.853 and 0.67 millimolar solutions respectively. With the latter elements i_{d_2} changes less and less with concentration.

An insight into the mechanism of the reduction process may be gained from a study of the waves, particularly from calculations of the diffusion current constants i_{d_1} and i_{d_2}; it has however to be borne in mind that i_{d_2} involves a large uncertainty in view of the diffuse appearance of the second wave. These constants were computed employing the Ilkovic equation as modified by LINGANE AND LOVERIDGE[6] in which the correction factor was set equal to 1.1. i_{d_1} and i_{d_2} may also be computed theoretically from the relation $i_d = 607 \times n \times D_2^{\frac{1}{2}}$. D in this equation is usually assumed to be equal to D_i° calculated from equivalent conductance, λ° at infinite dilution assuming once again the relation $D_i^{\circ} = 2.7 \cdot 10^{-7} \frac{\lambda_{\circ}}{z}$ ('z' the number of charges on the ion). The very precise data of SPEDDING[7] on the equivalent conductances of rare-earth ions enable a fair evaluation of D°_i and hence i_d. These are shown in Table IV. The value of D°_i ranges between 5.669 to 6.209 × 10^{-6} cm² sec⁻¹ for these elements. One obtains on the basis of a 'one' electron change in the first wave for i_{d_1}, a value in the neighborhood of 1.5 while the experimental values for i_{d_1} range from 3.31 to 3.71 average about 3.40. In the same table are also shown the reciprocals of the slopes of the plots of log $\frac{i}{i_d - i}$ *vs.* Ed.e. for the first wave. Its theoretical value for a one electron change is 0.059 and for a three electron change 0.02.

TABLE IV

Element	$\lambda_{\circ}$ for R^{+3} ohms^{-1} cm^2	$D_i^{\circ} \times 10^{-6}$ cm^2 sec^{-1}	i_{d_1}	i_{d_2}	Reciprocal slope of log $\frac{i}{i_d - i}$ *vs.* Ed.e.
La	69.76	6.209	3.31	6.97	0.047
Pr	69.66	6.198	3.48	7.32	0.046
Nd	69.46	6.183	3.43	7.29	0.044
Sm	68.56	6.102	3.43	7.13a 4.31b	0.050
Gd	67.36	5.995	3.66	7.75a 3.58b	0.047
Dy	65.66	5.843	3.51	7.09a 2.48b	0.047
Y	63.70*	5.669	3.70	7.95a 4.21b	0.049

a. Highest concentration of the element studied
b. Lowest concentration of the element studied.
*. Derived from the equivalent conductance of yttrium sulphate.

The experimental value for i_{d_1} is about twice the theoretical. The same discrepancy may be noticed in i_{d_2} values as well when normal second waves were registered. This may be due to the irreversibility of the process and to the regeneration of M^{+3} from M^{+2} (*vide infra*). The reciprocal of the slope of the plot of log $\frac{i}{i_d - i}$ *vs.* Ed.e, also has a value around 0.05 which is in fair agreement with the one for one-electron change.

It is further of interest that the average diffusion current per millimole per litre in the first stage of reduction is nearly the same for all the rare earths studied — averaging about 5.0 μA for the electrode system employed.

The two waves represent thus the step-wise reduction process $M^{+3} \rightleftarrows M^{+2} \leftrightarrows M^{\circ}$. The diffusion current values bear this out unequivocally in the case of La, Pr and Nd. The polarograms of all the elements studied are similar; they only differ in the heights of the second waves. TIMNICK AND GLOCKLER[4] in their studies of samarium waves determined i_{d_1} and i_{d_2}. In a one millimolar solution, they obtained the values 3.85 and 8.2 and in 4 millimolar 3.50 and 2.93 respectively. These may be compared with those noted in Table IV; *viz*, i_{d_1} 3.43 in all concentrations and i_{d_2} 7.13 in 0.8 millimolar and 4.31 in 3 millimolar solutions. The first wave in samarium has been assigned by these investigators to reduction to $^{+}2$ state. What holds for samarium will hold for other elements equally well.

It remains now to explain the anomalous diffusion currents in the second waves of Sm—Y. This anomaly becomes greater with concentration as well as decrease in basicity. This behaviour is indeed difficult to explain completely without further data. The two observations that the pH of the solution increases and i_{d_2} values fall off more and more from expected ones as the concentration increases, furnish a clue to qualitative understanding. The principal electrode reactions are

$$M^{+3} + e \rightarrow M^{+2} \quad \text{(First wave)}$$
$$M^{+2} + 2e \rightarrow M \quad \text{(Second wave)}$$

However M^{+2} is unstable in a number of cases. The disturbing reaction

$$M^{+2} + H_2O \rightarrow M^{+3} + OH^- + H$$

in which M^{+3} ion is regenerated increases the pH through liberation of OH^- ions. While the regeneration of M^{+3} tends to increase the diffusion current and affect the heights of both the waves, the production of hydroxyl ions has two mutually opposing effects on the second wave. On the one hand, the hydroxyl ions by combining with the metal ions (M^{+3} or M^{+2}) produce the hydroxide and remove the ions from the solution with a consequent reduction in the diffusion current. On the other hand, to whatever extent the hydroxide is soluble in water, the reduction in difusion current is counteracted. It is probable with La, Pr and Nd, that these opposing effects just balance, giving second waves in conformity with theory. In the case of Sm-Y however, the solubilities of these hydroxides or hydrous oxides are much less and the reduction factor outweighs them, resulting in a reduction of the total diffusion current. MOELLER AND KREMERS[8] have investigated the

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water solubilities of the rare-earth hydroxides, which however appear to be of the same order of magnitude though differing sensibly — $7.8 \cdot 10^{-6}$ moles g/litre for La and $1.2 \cdot 10^{-6}$ g moles/litre for Y at the other end. It is difficult to presume that these differences can account for the large variations in diffusion current characteristics. Other processes may also be at work. It is likely that the rare-earth elements do not form soluble amalgams on the mercury surface but are simply adsorbed. Adsorption lowers the diffusion current. What one observes is the cumulative effect.

The comment of KOLTHOFF AND LINGANE[9] that the first wave in the experiments of NODDACK AND BRUKL[2] might have been due to catalytic hydrogen discharge is not applicable here. The first wave, in all the polarograms presented here, has none of the characteristics of catalytic hydrogen discharge, *i.e.* (a) increase in height with increase in hydrogen ion concentration and (b) irregular rise with concentration of the substance giving rise to the wave. Besides, a separate hydrogen wave appears in each picture. The height of the hydrogen wave was also noticed to increase linearly with hydrogen ion concentration (polarograms not shown).

The half-wave potentials of the two steps, though they differ narrowly, nevertheless present some regularity. These values, at the same, or very nearly the same, pH are shown in Table V.

TABLE V

$E_{\frac{1}{2}}$ *vs.* S.C.E. OF THE TWO STEPS AT THE SAME pH IN 0.1*N* LICL AND 0.01% GELATIN AT 30 ± 0.05° C

Elements	pH	$Ea_{\frac{1}{2}}$ First step	$Eb_{\frac{1}{2}}$ Second step	($Eb_{\frac{1}{2}}$ △E = — $Ea_{\frac{1}{2}}$)
		Volts	Volts	Volts
La	3.16	—1.895	—2.030	—0.135
Pr	3.10	—1.846	—1.995	—0.149
Na	3.07	—1.850	—2.014	—p.164
Sm	3.10	—1.818a	—1.985	—0.167
Gd	3.10	—1.852	—1.989	—0.137
Dy	3.09	—1.793	—1.941	—0.148
Y	3.08	—1.846	—1.983	—0.137
Sc	3.12	—1.693b	—	single wave

(a) *Cf.* TIMNICK AND GLOCKLER[4] — —1.80 v. and —1.96 v. *vs.* S.C.E. respectively.
(b) *Cf.* LEACH AND TERREY[3] —1.80 v. *vs.* S.C.E.

The △E values noted in the last column of Table V possess some interest. In the two series La-Gd and Gd-Lu, the pattern appears to repeat itself, although fuller data alone would justify any definite conclusion. However in La and Gd, both with *one* 5 d electron this value is almost the same *viz.* —0.135 and —0.137 v *vs.* S.C.E.; the same difference occurs even in yttrium which has a single

4 d electron. In Pr and Dy, two elements similarly situated, one sees again a constancy of this difference —0.148 V. Similarly in holmium the difference may be expected to lie around —0.164 volts as observed in the case of neodymium.

In this connection it is of interest to note the findings of ZARINSKII[10], who failed to obtain a second wave with sulphate solutions of Pr, Nd and Sm, while with the chlorides in 0.1*N* LiCl a preliminary reduction to the bivalent state was noticed. A copy of this publication could not be obtained.

One of the authors (A.P.) thanks the Government of India for the award of a Senior Scholarship which enabled this work to be carried out.

SUMMARY

From a study of the polarograms of chlorides of lanthanum, praseodymium, neodymium, samarium, gadolinium, dysprosium and yttrium in 0.1*N* lithium chloride together with 0.01 % gelatin as maximum suppressor, it has been shown that the reduction proceeds in two stages.

$$M^{+3} + e \rightleftharpoons M^{+2} \quad \text{and} \quad M^{+2} + 2e \rightleftharpoons M$$

In the case of the less basic elements, anomalies in the heights of the second steps have been observed and these anomalies have been qualitatively explained on the basis of disturbing electrode reactions. The half-wave potentials for each step have been listed.

Gelatin has not been found to be very efficient as a suppressor of maxima. In some cases a maximum is in evidence though partially.

RÉSUMÉ

L'étude des polarogrammes des chlorures de lanthane, de praséodyme, de néodyme, de samarium, de gadolinium, de dysprosium et d'yttrium dans LiCl 0.1*N* et en présence de 0.01% de gélatine („maximum suppressor") a montré que la réduction s'effectue en deux stades:

$$M^{+3} + e \rightleftharpoons M^{+2} \quad \text{et} \quad M^{+2} + 2e \rightleftharpoons M$$

Dans le cas des éléments moins basiques, on observe des anomalies dans les hauteurs du deuxième palier. Ces anomalies peuvent être qualitativement expliquées. Le potentiel de demi-onde ($E\frac{1}{2}$) de chaque saut a été vérifié. La gélatine s'est montrée peu efficace pour supprimer les maxima.

ZUSAMMENFASSUNG

Die Untersuchung der Polarogramme der Chlorverbindungen des Lanthans, Praseodyms, Neodyms, Samariums, Gadoliniums, Dysprosiums und Yttriums in 0.1*N* Lithium-chlorid und 0.01 % Gallerte als Hemmungskörper der Maxima zeigt, dass die Reduktion in zwei Stufen erfolgt:

$$M^{+3} + e \rightleftharpoons M^{+2} \quad \text{und} \quad M^{+2} + 2e \rightleftharpoons M$$

Bei minder-basischen Elementen hat der Verfasser Unregelmässigkeiten in den Höhen der zweiten Stufen bemerkt und erklärt diese auf Grund von störenden Elektrodenreaktionen. Die Halbwellenspannung für jede Stufe ist geprüft worden. Als Unterdrücker der Maxima hat sich die Gallerte nicht wirksam erwiesen. In einigen Fällen tritt ein Maximum, wenigstens teilweise hervor.

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ANALYSIS WITH THE ELECTRONIC POLAROSCOPE*

by

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In a previous communication[1] the analytical method of oscillographic polarography with alternating current has been described. The present paper is a continuation bringing new analytical applications. To facilitate the research in oscillographic polarography, the portable "Electronic Polaroscope" (Fig. 1) is being manufactured**. This apparatus shows on the screen the most suitable diagram $\frac{dV}{dt}$ against V, and it suffices to connect two terminals to the mercury cell and the other two to the mains.

The scheme of connections inside the instrument is shown in Fig. 2. From the mains (A.C.) of 50 Hz frequency the current is transformed to 220 V and led

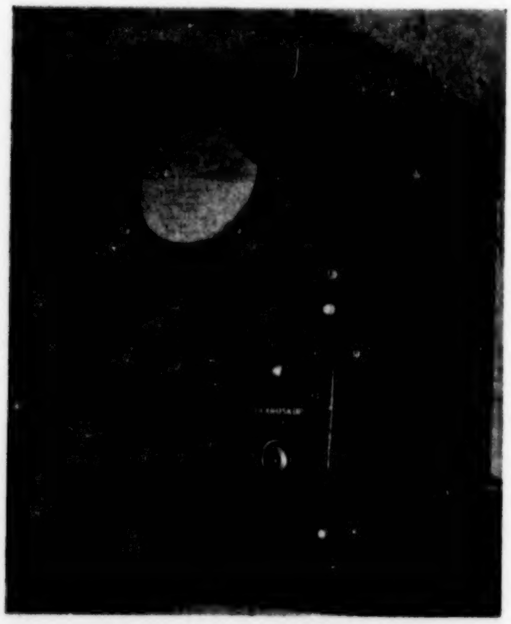

Fig. 1. The Electronic Polaroscope. Dimensions: 30 × 30 × 23 cm, weight: 18 kg.

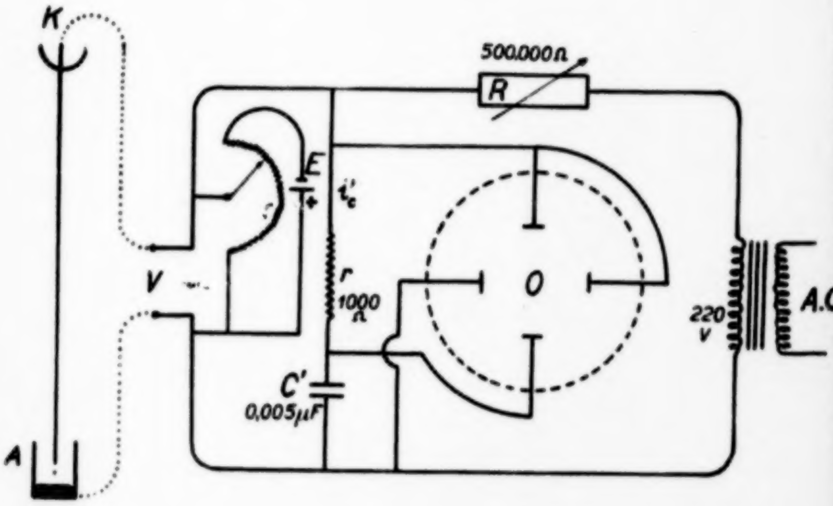

Fig. 2. Scheme of connections inside the polaroscope.

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* Paper read at the Symposium on Analytical Chemistry, held by the Midlands Society for Analytical Chemistry at Birmingham, 1954.

** National Enterprise KŘIŽIK-150, Prague-XVI, Plzeňská 96.

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through a variable resistance R (up to 0.5M Ohm) to the mercury electrodes of the polarographic cell (K is the capillary electrode, A the mercury reference electrode). Upon the alternating voltage a direct voltage is superimposed from the source E, so as to impart to the polarizable electrode the voltage V, alternating between 0 and —2 volt. The derivative link consists of a resistance r (*ca.* 1000 ohm) and a condensor of capacity c', about 0.005 μF, placed in parallel to the mercury cell. Then the current i'_c charging the condensor c', is equal to $\frac{dV}{dt} \cdot c'$. O represents the cathode ray oscilloscope with the two pairs of plates.

QUANTITATIVE DETERMINATION OF DEPOLARIZERS

The direct method of quantitative estimation in oscillographic polarography with alternating current is that of recording the derivative-time curve, $\frac{dV}{dt} - t$ (Fig. 3). As has been already pointed out[2], the number of coulombs passed through the mercury cell when the depolarizer is electrolyzed, is proportional to the area A ($= A'$) of the cut-in caused by electrolytic current, i_E. Then A is also proportional to the concentration of the depolarizer, and this dependence of A on the concentration may be obtained from a calibration curve; it is mostly linear.

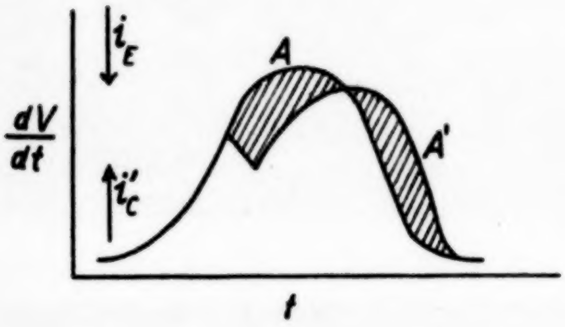

Fig. 3. The area A ($= A'$) of the cut-in on the $\frac{dV}{dt} - t$ curve.

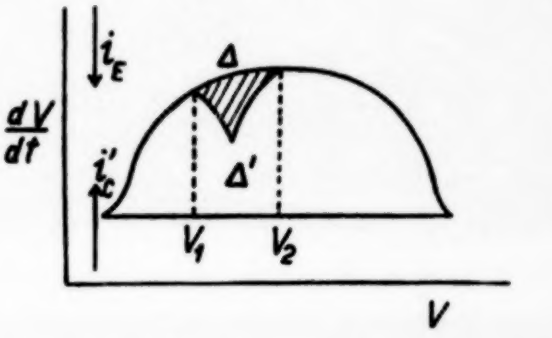

Fig. 4. The area $\triangle$ of the cut-in on the $\frac{dV}{dt} - V$ curve; $\triangle'$ is the complement of $\triangle$ between the ordinates at V_1 and V_2.

With the "electronic polaroscope", however, we get derivative-potential curves, $\frac{dV}{dt} - V$ (Fig. 4). Here the quantity of the depolarizer which is proportional to A, has to be calculated from the area of the cut-in, $\triangle$, in the following way:

A, according to Fig. 3 $= \bar{i}_E\ (t_2 - t_1)$, when $\bar{i}_E$ denotes the mean current due to electrolysis of the depolarizer during the time $t_2 - t_1$. Further, $\triangle$, according to Fig. 4 $= \bar{i}_E\ (V_2 - V_1)$, where $\bar{i}_E$ is again the mean electrolytic current as in Fig. 3, and V_2 and V_1 the potentials between which the cut appears. Thus $\frac{\triangle}{A} = \frac{V_2 - V_1}{t_2 - t_1}$; however, according to the function of the derivative link

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$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{V_2 - V_1}{t_2 - t_1} = \frac{\overline{i'_c}}{c'}$ where $\overline{i'_c}$ is the mean charging current giving the ordinate.

$$\text{Hence } \frac{\triangle}{A} = \frac{\overline{i'_c}}{c'}, \text{ or } A = \triangle \cdot \frac{c'}{\overline{i'_c}} = \frac{\triangle . c'(V_2 - V_1)}{\overline{i'_c}\,(V_2 - V_1)}.$$

According to Fig. 4 the product $\overline{i'_c}\,(V_2 - V_1)$ is the area determined by the cut-in and by the ordinates at V_2 and V_1 denoted $\triangle'$.

Therefore $A = \frac{\triangle}{\triangle'}(V_2 - V_1) \cdot c'$.

To evaluate the areas, the luminous diagrams have to be photographed; this is easily carried out with the streaming mercury electrode, which gives stable curves. These diagrams are usually simpler than those obtained with the dropping electrode, since at the dropping electrode consecutive and side-reactions may occur. These are, however, often very characteristic for the quality of the depolarizer. To obtain stable luminous diagrams also with the dropping electrode, **Kalvoda**

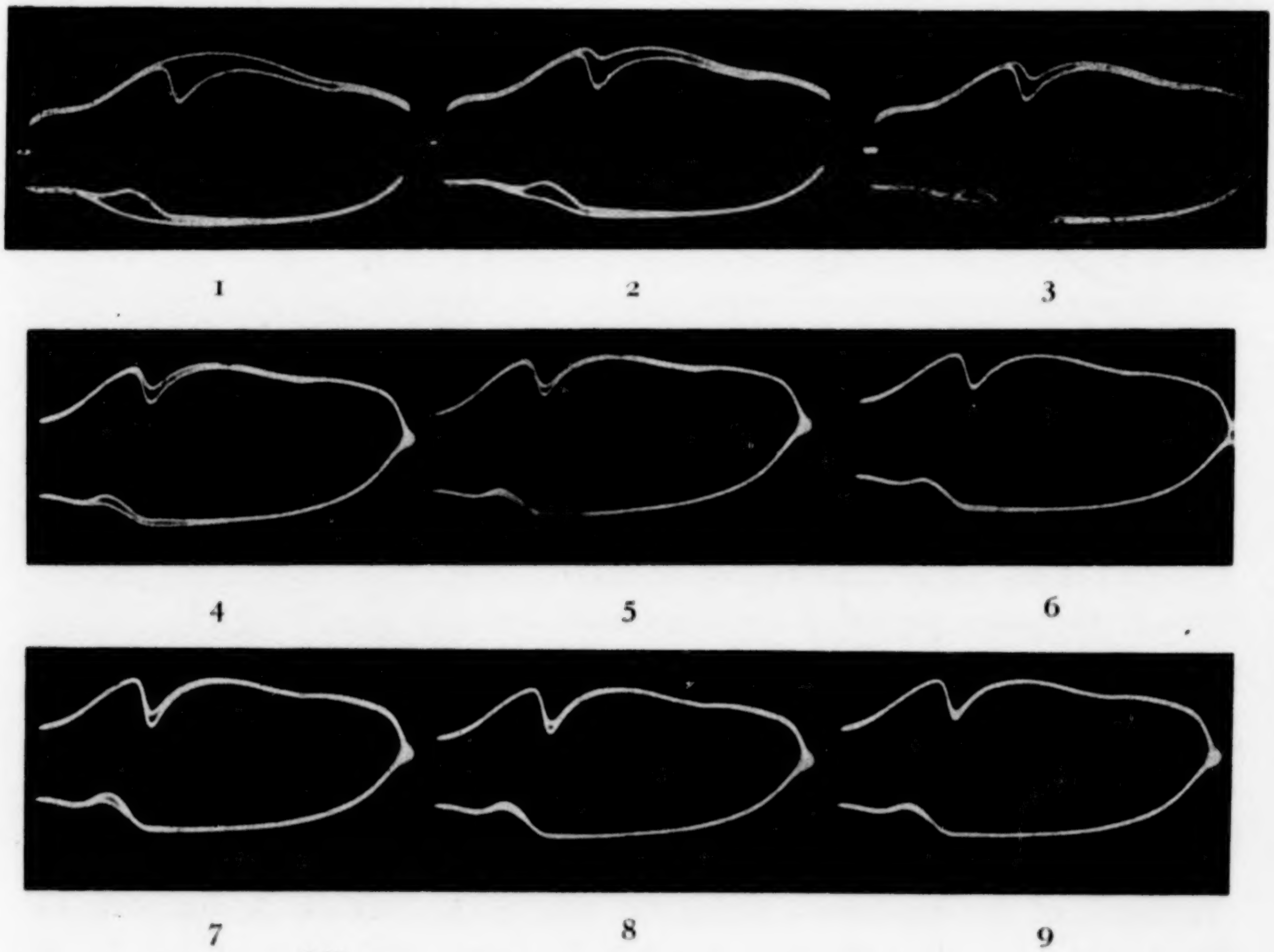

Fig. 5. Diagrams $\frac{\mathrm{d}V}{\mathrm{d}t} - V$. Oscillographic subtractive titration. One solution of $1\,M$ KCl contains 0.25 mg Cd^{+2}, into the other solution of $1\,M$ KCl were successively added 0; 0.05; 0.10; 0.15; 0.20; 0.25; 0.30; 0.35; 0.40 mg Cd^{+2}.

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AND MACKU have recently[3] made an arrangement, in which they illuminate the diagram on the luminous screen exactly at the same moment of the formation of the drops, about 1 sec after the fall of the previous drop. The rate of dropping is regulated by automatic tapping. Such diagrams then coincide perfectly and if the afterglow at the screen is sufficiently long, the diagrams fuse into one stable figure. Thus we may at any instant of the growing mercury drop follow the rate of exhaustion of the depolarizer at the surface of the drop, or study the formation of the active products of the electrolysis.

Recently, KALVODA AND MACKU[4] have introduced for quantitative measurements a comparative titration method, by which they project on oscilloscope alternatively every 1/25th of a sec the diagram of the solution with the component to be determined and that of the pure basic electrolyte. Twin dropping mercury electrodes are necessary and mechanical tapping to keep the dropping perfectly synchronous. The component to be determined is added by drops to the solution of the pure electrolyte, until both curves coincide (Fig. 5). The solution to be analysed is in this sort of comparative titration kept unchanged. The results are precise within 3%.

PHARMACEUTICAL PRODUCTS

In the manner given above, *viz.* with the stable picture at the dropping mercury electrode, diagrams characterizing various sulphonamides were obtained[5], *e.g.* of sulphadimidin, sulphadiazin and sulphaguanidin, which may be distinguished also in their mixture (Fig. 6) in the drug Detrion. Here the electrolyte was $1M$ H_2SO_4 and the sulphonamides 6 to $8 \cdot 10^{-4}M$.

Also sulphapyridin, sulphathiazol and globucid (*p*-aminobenzene-sulphonamide-ethyl-thiodiazol) give in $1M$ H_2SO_4 characteristic diagrams. Amongst local anaesthetics, procain, intercain and nupercain (percain) are oscillographically active. Intercain and nupercain can be distinguished in their mixture (Fig. 7); this is of importance as nupercain is one of the most efficient and most toxic of local anaesthetics. Similarly many acridin derivatives are well shown in the buffer of $1M$ acetic acid and $1M$ acetate.

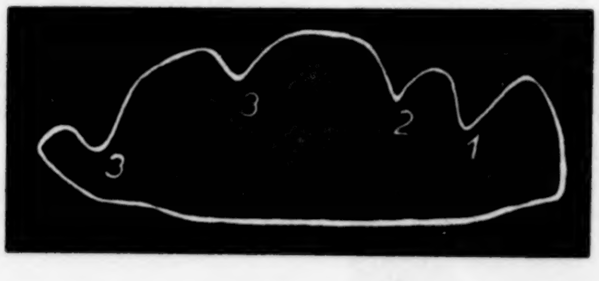

Fig. 6. Oscillogram of a mixture containing 6 to $8 \cdot 10^{-4}M$ sulphadimidine (1), sulphadiazine (2), and sulphaguanidine (3), in $1M$ H_2SO_4.

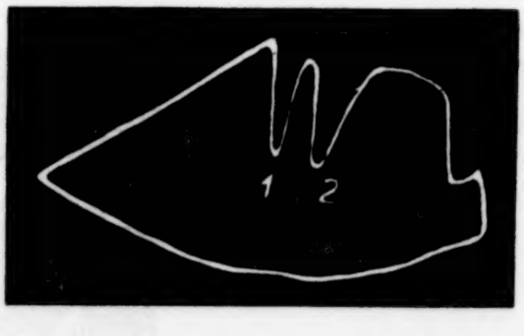

Fig. 7. Oscillogram of a mixture of $5 \cdot 10^{-4}M$ intercaine (2) and nupercaine (percaine) (1) in $1M$ H_2SO_4.

Of the commonly used alkaloids, papaverin, codein and pilocarpin give a cut-in at —1.6 V in 1N LiOH. A solution of physostigmin in 1M KOH (0.003% of its salicylate) is, when freshly prepared, colourless (Fig. 8a); after a minute the solution turns red, due to the change to rubreserin; simultaneously the two cathodic cuts at negative potentials disappear (Fig. 8b, c). Oscillographic polarography in general may be helpful in the analysis of mixtures of various alkaloids and other drugs, even when some of them are inactive.

In purine derivatives the way of distinguishing traces of phenobarbital in barbital is noteworthy. If the mixture is nitrated in a test-tube by dipping it

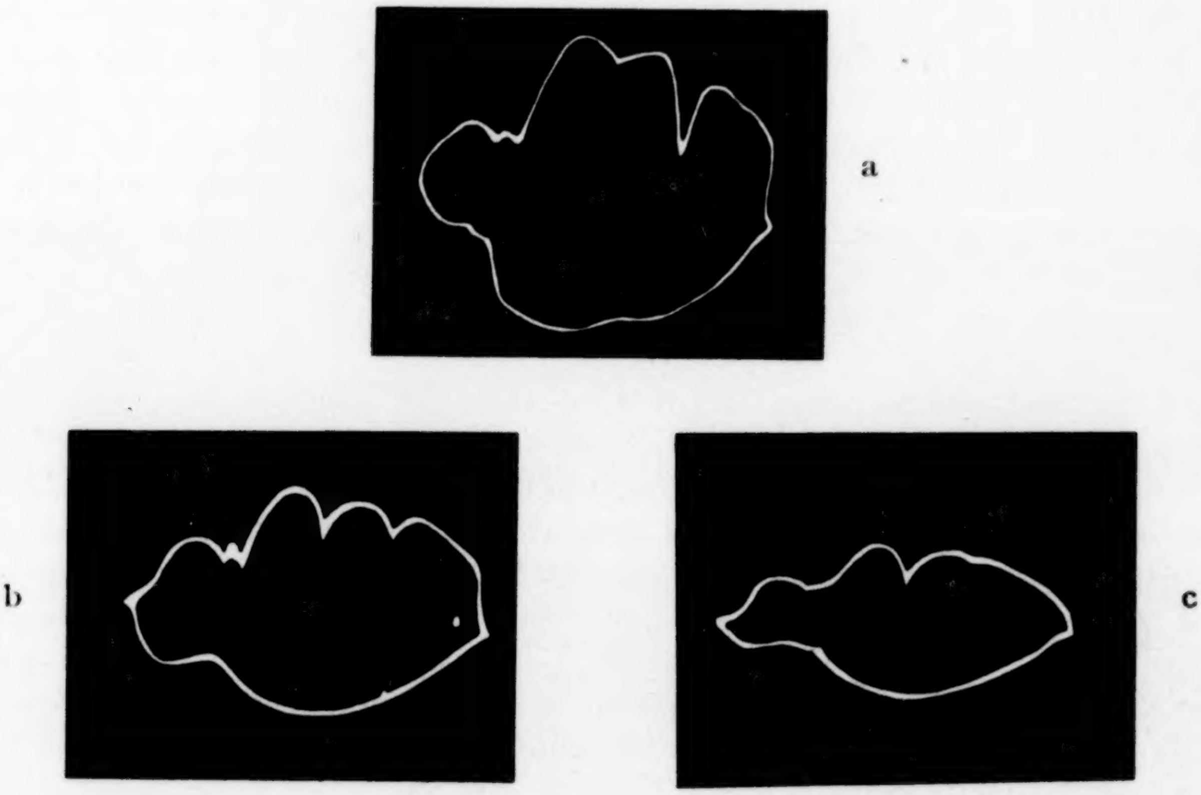

Fig. 8. Oscillograms of a solution of $1.4 \cdot 10^{-4} M$ physostigmin salicylate in 1M KOH: a) freshly prepared, b) after 30 sec, c) after 3 min.

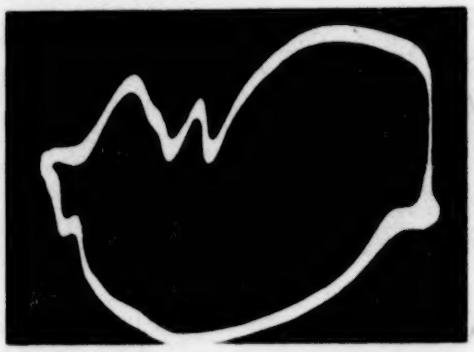

Fig. 9. Oscillogram of a mixture of phenobarbital in excess of barbital after nitration, in alkaline solution.

for 1 to 2 minutes into boiling water and the contents are then made alkaline, the ensuing solution shows only the nitrated phenobarbital (Fig. 9).

A further mixture of two related substances to be oscillographically easily resolved is 1-hydrazinophthalazine and 1-4-dihydrazinophthalazine[6] (Apresolin and Nepresol, CIBA), which are well shown at the dropping electrode as well as at the streaming one.

From pyridin derivatives, besides the three isomers of nicotinic acid mentioned previously[1], VOLKE AND VOLKOVA[7] describe trigonellin, nicotin, dipicolinic, dinicotinic and *iso*cinchomeronic acids.

According to MOLNÁR AND BAUER[8], traces of benzaldehyde in technical 1-phenyl-acetylcarbinol, prepared from benzaldehyde by fermentation, are oscillographically quickly determinable.

ARTEFACTS

In the electrolysis using alternating current, substances may be oxidized at extremely positive potentials or form compounds with mercury, which is anodically dissolved. In an analogous manner they may be reduced at extremely negative potentials, and the compounds thus formed can act as depolarizers. We call the substances artificially prepared in this way "artefacts". *e.g.* carbon disulphide is reduced at —1.5 V (from N.C.E.) to sulphide ions, which act as depolarizers, forming with mercury insoluble compounds. Also penicillin[9], whilst coming in contact with the mercury ions at positive potentials, is isomerized into penicillenic acid, which forms a prominent cut-in at —1.0 V.

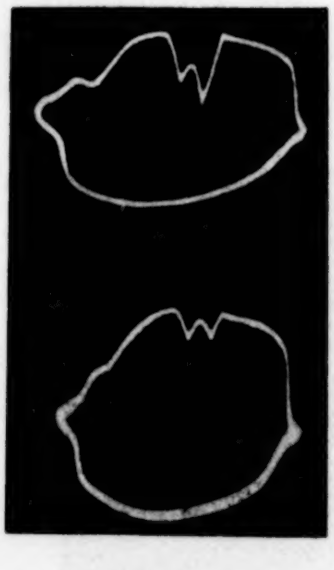

Fig. 10. Oscillogram showing the presence of acetylene in 5*M* KOH. Above: at the dropping electrode. Below: at the slowly streaming electrode.

The oscillographic indication of artefacts is shown best at the dropping mercury electrode; at the streaming electrode the artefacts as well as all other products of electrolysis are carried away from the electrode.

Recently acetylene has been found oscillographically active through an artefact. The isolated unsaturated bond of acetylene cannot be hydrogenated in electrolysis with the dropping mercury electrode. However, when some bubbles of acetylene are passed through a strongly alkaline solution (5*M* KOH), oscillographic analysis shows marked cuts (Fig. 10). Closer examination reveals that the depolarizer giving this effect is formed at extremely positive potentials, and that it is therefore due to the ions of mercury, which at those potentials pass into solution. Acetylene is known to form in alkaline medium acetylides, such as $\underset{\diagdown \mathrm{Hg} \diagup}{\mathrm{C} \equiv \mathrm{C}}$,

$HgC \equiv CHg$, $HC \equiv C\text{-}Hg$ or $Hg\text{-}C \equiv C\text{-}Hg\text{-}OH$, in which mercury is bound organically by homogeneous links. We may then expect irreversible electrodeposition of mercury at rather negative potentials. Anodically there is, of course, no effect shown, as the reaction occurs at very positive potentials, where the dissolution of mercury leads to the formation of acetylides. It might be thought that this oscillographic effect is due to phosphine, which — as an impurity — imparts to acetylene the evil smell. Acetylene was therefore purified until it had no odour; the oscillographic cuts remained unchanged. On the other hand, when phosphine gas was passed through the alkaline solution containing some acetylene, it did not effect any new cut-in on the oscilloscopic diagram; after prolonged bubbling phosphine even caused a decrease of the acetylene effect, evidently because the passage of the indifferent gas (PH_3) removes acetylene from the solution. In Fig. 10 the upper diagram was obtained at the dropping electrode whilst the lower diagram is due to the slowly streaming electrode, when the mercury reservoir is kept low. As the reservoir is raised, the effects gradually disappear, because the artefacts are now carried away from the electrode by the quick stream of mercury.

VITAMINS AND ANTIBIOTICS

ČERNÝ* has oscillographically investigated the behaviour of the vitamins belonging to the B group and of some antibiotics, and showed that many of them may be qualitatively as well as quantitatively determined even in their mixtures and in biological material, *e.g.*, nicotinic acid and its amide (Fig. 11), vitamin B_2 (lactoflavin or riboflavin) (Fig. 12) in $1M$ H_2SO_4; its photolysis in $1M$ KOH (Fig. 13). Folic acid or vitamin B_C(pteroyl glutamic) shows in $1M$ H_2SO_4 a marked

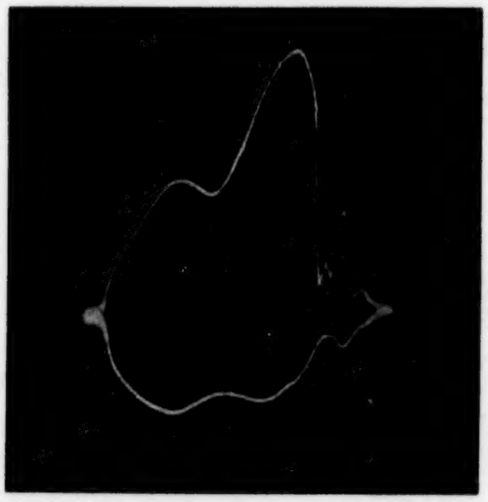

Fig. 11. The double cut-in of nicotinic acid (left) and its amide (right), in $1M$ H_2SO_4.

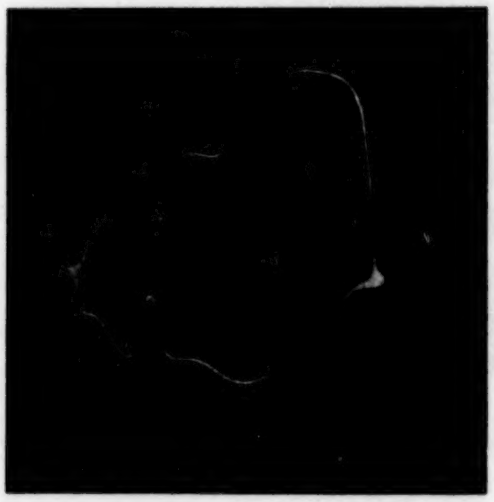

Fig. 12. Vitamin B_2 in $1M$ H_2SO_4.

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* Reported in a lecture at the Czechoslovak Chemical Society, Prague, April 27th, 1954.

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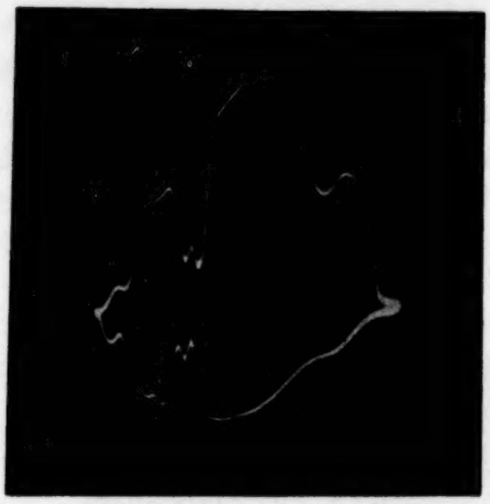

Fig. 13. Beginning photolysis of vitamin B_2 in 1*M* KOH. The reversible cut-in is split into two.

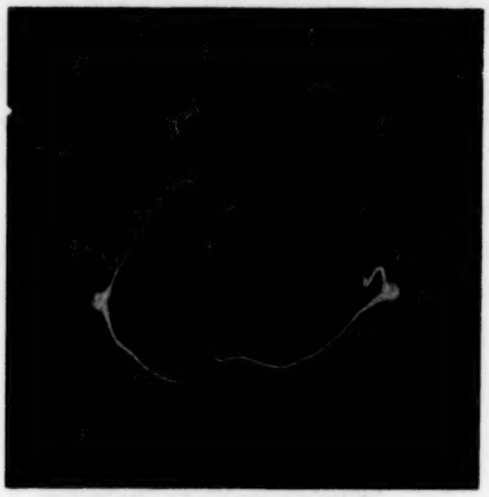

Fig. 14. Folic acid in 1*M* H_2SO_4 at the streaming electrode.

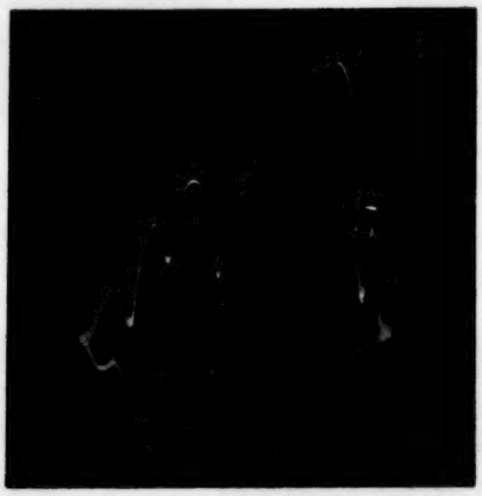

Fig. 15. Mixture of vitamins B_1 (aneurin) (first pair of cuts), B_2 (second pair of cuts), and B_c (third pair of cuts), in 1*M* H_2SO_4. The fourth, irreversible cut-in to the right is due to catalytic evolution of hydrogen caused by B_1.

reversible cut-in (Fig. 14) similar to that of lactoflavin, but at a more negative potential. Thus we may distinguish in a mixture vitamin B_1(aneurin), B_2 and B_c (Fig. 15).

Vitamin B_{12} (cobalamine) is clearly shown in solutions of 1*M* H_2SO_4 or 1*M* NaOH when added either from pure crystalline specimens or from injections with liver extracts (Fig. 16).

Fig. 17 shows the diagram of chloromycetin and its difference from aureomycin (Fig. 18). All these pictures were obtained with the streaming mercury electrode. The dropping mercury electrode gives more complicated diagrams, *e.g.* Fig. 19, of folic acid (compare with Fig. 14); the new cuts are due to consecutive or side reaction, however, the chief reversible cut-in is identical at both capillary electrodes. ČERNÝ has also shown that biological material, *e.g.* flour, soil or residues after fermentation are no obstacles to the clearness of the diagrams.

Finally, the results of MOLNÁR** should be mentioned, who found characteristic oscillographic curves with 3- and 17-ketosteroids. Those with a conjugated double linkage to the carbonyl group, *e.g.* testosteron and desoxycorticosteron are both

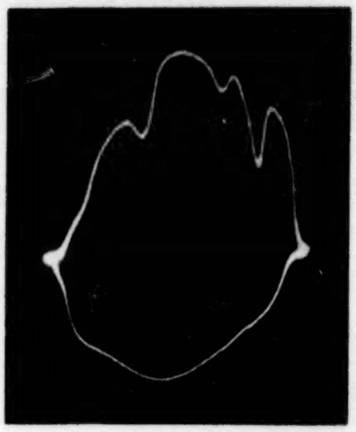

Fig. 16. Vitamin B_{12} (cobalamine) from liver extracts in 1M KOH.

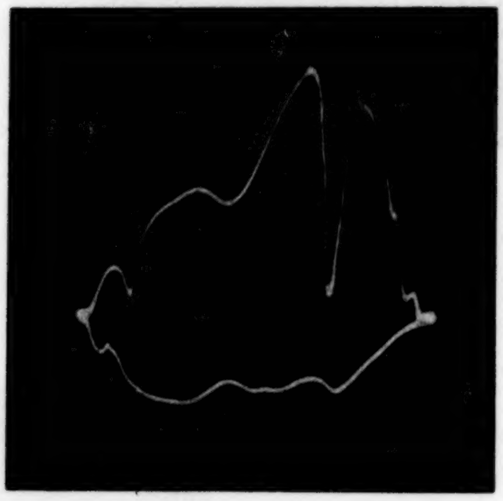

Fig. 17. Aureomycin in 1M H_2SO_4.

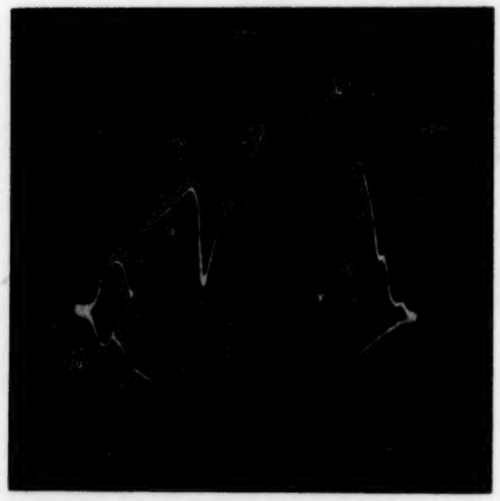

Fig. 18. Chloromycetin (the two cuts on the left) and aureomycin (the deep cut-in to the right) in 1M H_2SO_4.

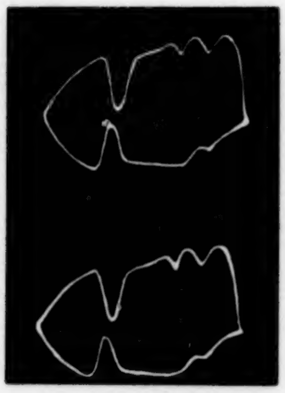

Fig. 19. Folic acid at the dropping mercury electrode (taken twice to show the reproducibility), in 1M H_2SO_4.

** Communicated to the Congress of Theoretical Polarography, Smolenice June 1954.

References p. 609.

polarographically and oscillographically active. Ketosteroids with the isolated keto-group, like oestron and dehydroisoandrosteron give polarographically no effect, but oscillographically are active, probably through the formation of artefacts. As these substances are but slightly soluble in water, 20% alcohol was added. The effect is shown down to a concentration $2 \cdot 10^{-5} M$.

SUMMARY

Analysis by means of oscillographic polarography with alternating current is discussed and illustrated by luminous diagrams showing the dependence $\frac{dV}{dt} - V$. The quantity of the depolarizer can be determined either by the area of the cut-in on the diagram or by a comparative titration method.

Practical examples are given in oscillographic analysis of various sulphonamides, local anaesthetics, purine derivatives, alkaloids, pyridin carboxylic acids, vitamins, antibiotics, hormones, *etc.*

RÉSUMÉ

L'analyse par polarographie oscillographique, en courant alternatif, est discutée et illustrée de photographies, (diagrammes obtenus sur l'oscilloscope) démontrant la relation $\frac{dV}{dt} - V$. La quantité de dépolarisant peut être déterminée, soit par la surface de l'encoche, soit par une méthode de titration comparative. Des exemples pratiques sont donnés: analyse oscillographique de divers sulfamidés, d'anesthésiques locaux, de dérivés de la purine, d'alcaloïdes, d'acides pyridine-carboxyliques, de vitamines, d'antibiotiques, d'hormones, *etc.*

ZUSAMMENFASSUNG

Die oszillographisch-polarographische Analyse mit Wechselstrom wird besprochen und die Abhängigkeit $\frac{dV}{dt} - V$ durch veranschaulichende Leuchtdiagramme illustriert. Die Quantität des Depolarisators kann entweder aus der Fläche des Einschnittes am Diagramm oder durch eine vergleichende Titrationsmethode ermittelt werden.

Es werden praktische Beispiele der oszillographischen Analyse verschiedener Sulfonamide, Lokalanästhetika, Purinderivate, Alkaloide, Pyridincarboxylsäuren, Vitamine, Antibiotika, Hormone, usw. angeführt.

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BOOK REVIEWS

The Identification of Organic Compounds, 4th Edition (1st English Edition), by STIG VEIBEL, G. E. C. Gad, Copenhagen, 1954. XV + 346 pages, 26 fig. Price 45 s.

The book was written for degree students at the University of Copenhagen and originated 26 years ago. Its subtitle is *A manual of qualitative and quantitative methods* and its scope is, therefore, appreciably greater than might be gathered from the main title.

A good feature is that at the very commencement it is stressed that the purity of the unknown substance should be examined, and if necessary purification effected before proceeding. Determinations of the usual criteria — melting point, boiling point, etc., are described, and methods for purification, including chromatography and ion exchange, discussed (16 pages). There follow three more sections: detection and determination of the elements (30 pages), preliminary examination and general tests (9 pages) and detection and estimation (the Reviewer would prefer the word "determination") of functional groups (299 pages). The last section is obviously the most important one of the book and deals with (1) the hydroxyl group, (2) the carbonyl group, (3) carbohydrates, (4) carboxylic acids, (5) esters, (6) alkoxyl compounds, (7) amines, (8) amino acids, (9) amides, (10) nitriles and *iso*cyanides, (11) diazo compounds, (12) azo compounds, (13) azoxy compounds, (14) hydrazines, (15) nitro compounds, (16) nitroso and *iso*nitroso compounds, (17) substituted hydroxylamines, (18) substances containing active oxygen, *e.g.* peroxides and quinones, (19) halogen compounds, (20) sulphurcontaining substances, (21) the double bond (22) the triple bond, (23) hydrocarbons.

The book may be considered as successfully dealing, at least in outline, with an enormous field within a reasonable space. Compression has necessarily been inevitable, but very full (and up-to-date) references to the original literature are given. In the Reviewer's opinion, the book will prove not only of great value to University students but also to industrial organic chemists who have occasion to ascertain the identity and/or purity of organic substances.

The English is good, no doubt helped by the collaboration of Dr. P. SYKES of Cambridge University Chemical Laboratory.

N. STRAFFORD (Manchester)

English for the Scientist par CLÉMENT DUVAL, Maître de Recherches au C.N.R.S. (Editions Centre National de la Recherche Scientifique), 13, Quai Anatole France, Paris, 1954 (4ème édition), 96 pages, prix 450 fr.f.

La teneur de ce petit livre consiste en une méthode d'enseignement de l'anglais, dans le cadre de „*L'enseignement technique préparatoire à la recherche*". En particulier, il sert d'outil pour le cours au C.N.R.S. du Professeur CLÉMENT DUVAL, destiné, au perfectionnement des étudiants sachant déjà l'anglais littéraire.

Chaque leçon comporte un vocabulaire technique adapté à tel ou tel sujet: photographie, état des corps, analyse chimique, par exemple. Puis, dans des phrases détachées, ce vocabulaire est mis en oeuvre. Enfin des textes en anglais d'auteurs célèbres (EINSTEIN, RUSSELL, SODDY, LORD RAYLEIGH) sont proposés pour être expliqués. Parfois un thème termine la leçon.

Cet ouvrage se recommande en vue de la culture de l'anglais pour la compréhension des textes scientifiques, car tel est bien tout d'abord son but. Par son vocabulaire il sera en outre utile aux chercheurs même déjà familiarisés avec cette langue et qui seraient en présence de termes techniques inconnus d'eux.

M. JEAN (Paris)

The Optical Properties of Organic Compounds (Second Edition), by A. N. Winchell. Academic Press Inc., New York, 1954. xviii + 487 pp., 153 fig., $ 12.

This book is essentially a catalogue of more than 2,500 organic compounds which can be identified by optical properties, the most important of which are the indices of refraction. Nearly all crystallised organic compounds have two or three indices of refraction and these can be measured microscopically. The measurement of optical properties goes far towards the identification of a substance, provided, of course, that these properties have been measured previously on samples of known substances.

In the first section of the book the compounds are arranged according to the Beilstein system; data are given on optical properties and, in many cases, morphology, polymorphism, melting point and density. There are over 630 literature references.

In the next section there are two determinative tables; in these the compounds are listed in the order of highest and lowest measured refractive index respectively. In addition, there are two charts on which many of the compounds are placed: the first is based on refringence, birefringence and optic sign, the second on refringence and optic angle. The tables and charts are intended to assist identification from optical properties.

The book, which has obviously been compiled with great care, is a convenient source of information on optical properties of many organic compounds. It will also be of some value as a potential (or supplementary) means of identifying an unknown, provided it is always realised that the number of organic substances is so enormous that identification by physical properties, such as melting point and refractive indices, has only a limited chance of success.

N. Strafford (Manchester)

Substances Naturelles de Synthèse, Volume V, comportant la table récapitulative des cinq premiers volumes. Publié sous la direction de Leon Velluz par J. Mathieu, A. Petit, P. Poirier et L. Velluz, Masson et Cie. 1953, 206 pages, deux planches hors-texte de microphotographies. Broché fr. 2305; cartonné toile fr. 2690.

L'ouvrage débute par une étude des calciférols et la préparation des vitamines D_2 et D_3, avec une intéressante note sur la photochimie des stéroïdes et un autre sur la condensation de Diels-Alder en série stéroïde. On traite ensuite, pas à pas, la synthèse de la papavérine suivant Kindler et Peschke avec une note sur la méthode de chlorométhylation de Blanc et sur la condensation de Perkin. La DL-phénylalanine fait alors l'objet d'une étude spéciale ainsi que son dédoublement. Le phtiocol dont on sait l'intérêt depuis son isolement du bacille tuberculeux, voit sa synthèse effectuée suivant la méthode de Fieser, suivie d'une note sur la méthode de Thiele d'acétoxylation des quinones.

Nous trouvons encore l'importante synthèse de la vitamine K_1 par Fieser, puis celle du phytol.

L'intérêt de ce volume ne tarit pas lorsqu'on passe aux notes pratiques; cette fois nous sommes favorisés avec la cyclisation benzopyridique avec son tableau récapitulatif annexe et par une étude pratique de la chromatographie de partage; on donne de nombreuses valeurs de R_F et la carte des amino-acides.

L'ouvrage se termine sur la présentation d'une quinzaine de réactifs de condensation diénique. C'est un lieu commun de dire que cette collection est très importante, instructive et bien présentée. Les neuf premiers volumes ont déjà une belle carrière. Ils ont été écrits surtout pour le biologiste, mais je crois que l'analyste pourra trouver là des réactifs intéressants un jour ou l'autre. Il saura comment les préparer.

C. Duval (Paris)

SOME RECENTLY PUBLISHED BOOKS

L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen, London, 35*s*.

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